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Final Technical Report

Josephson Effect Research in High-Temperature Superconductors

Period of Report : 30 Sep 87 - 29 Sep 88

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Agency : U.S. Navy (ONR/SDIO)

Contractor: Wayne State University

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The original research proposal to ONR/SDIO had outlined two major goals to be accomplished during the three and half~~(3-1/2)~~ year period from July 1987 to December 1990. The first task was (i) the fabrication and characterization of thin film superconductors with the high-temperature oxide materials and secondly was (ii) the fabrication and characterization of Josephson tunnel junctions. These tasks included the following:

(i) fabrication and characterization of thin film superconductors:
- expansion of film techniques available
- reduction of substrate interactions on Si & alumina substrates
- correlation of film's properties with fabrication & processing conditions, including:
  types &temperature of substrates,
  oxidation & annealing treatment,
  degradation effects,
  composition variation, and
  metallic coating
- characterization of structural & superconducting properties, including:
  electrical resistance,
  I-V characteristics and critical current measurements,
  microwave effects on electrical properties,
  ac susceptibility and magnetization measurements,and
  XRD and SEM characterizations of crystalline and granular structure and composition analysis

(ii) fabrication and characterization of Josephson tunnel junctions:
- fabrication & characterization of granular Josephson-coupled network
- fabrication of "simple" Josephson junction [SIS,SNS,SSS microbridge]
- characterization of Josephson junction, including:
  nature of superconductivity,
  electromagnetic response, and
  dynamic properties

Although the administration/contracting of funds was not formally authorized until January 1988, the progress has been quite successful with regards to the first goal of fabrication and characterization of thin-film superconducting oxide films. Similar to all other research groups in being unable to fabricate simple Josephson tunnel junctions with superconducting oxides, we have however been able to initiate some characterization of the electromagnetic response observed in these films due to the inherent granular Josephson-coupled networks. In the following pages we outline in more detail the progress attained in the research proposal to date, a summary of the major accomplishments, an index of publications attributable to the present funding period, and the proposed program for continued research.

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Progress Report:

Fabrication and characterization of thin film superconductors:

e-beam evaporating system (rotatable four-source hearth):
sequential deposition of metals and fluorides, e.g., Cu - BaF_2-Y

[1] YBaCuO films on (11$\bar{2}$0) sapphire 1 μm thick

annealing procedure:
850 °C / 1 h + 550 °C / 1 h in moist O_2

microstructural characterizations:
SEM shows randomly oriented 123 rods (most in the plane of substrate)
dimensions of rods: 1-2 μm length
0.1-0.2 μm thickness
minimal degradation over eight months of storage

electrical characteristics:
T_{onset} : > 90 K
T_c : 68 K
I_o : $(T_c - T)^{3/2}$ suggests microbridges between grains
$I_o(4.2\text{ K})$: 3-5 x 10^3 A/cm^2

magnetic characteristics:
$T_{diamagnetism}$: > 65 K (λ_L>grain size for T>65 K)
χ_{ac} shows strong ac field dependence ($h_{perpendicular}$) which can be correlated to critical current density and strength of the Josephson coupling
χ_{ac} and M_{dc} shows strong orientation dependence of magnetic field h and film

microwave characteristics:
shift in I-V characteristics indicating novel dynamic states in oxide superconductors

[2] YBaCuO films on MgO and YZO (yttria-stabilized ZrO_2):
similar results as films on sapphire
more systematic studies of processing conditions needed

[3] BiCaSrCuO films on MgO
initial films lacked superconducting transition

rf triode sputtering deposition system (w/ Logothetis @ Ford):

sputtering from single source - target of prereacted, hot-pressed YBaCuO
- target of unreacted, hot-pressed Y_2O_3, $BaCO_3$, & CuO

[1] YBaCuO films on (11$\bar{2}$0) sapphire

deposition conditions:

unreacted target has <5% porosity and thus reduces outgassing and presputtering times
1-10 mTorr pressure
1-3% O_2 in Ar
substrate temperature of 450 °C
deposition rate of 100 A/min
thicknesses of 1-3 µm

annealing conditions:

800-900 °C / 1 h in flowing O_2 with slow cooling

microstructural characterizations:

SEM shows predominate 123 phase
x-ray fluorescence indicates 20% Cu deficiency

electrical characteristics:

T_{onset} : >90 K
T_c : 60 - 70 K
I_o (4.2 K) : 10^3 A/cm^2

[2] YBaCuO on Si and SiO_2 layer on Si

deposition conditions:

unreacted target has <5% porosity and thus reduces outgassing and presputtering times
1-10 mTorr pressure
1-3% O_2 in Ar
deposition rate of 100 A/min
thicknesses of 1-3 µm

annealing conditions:

rapid thermal processor (RTA) in O_2 for seconds

microstructural characterizations:

similar to sputtered films on sapphire
films degrade over several weeks

electrical characteristics:

T_{onset} : > 90 K
T_c : 46 K on Si after RTA @ 920 °C for 8 s in O_2
T_c : 50 K on SiO_2/Si after RTA @ 920 °C for 10 s in O_2
T_c : 66 K on SiO_2/Si after RTA @ 500 °C for 30 s in N_2 followed by RTA @ 920 °C for 10 s in O_2

microwave characteristics:

reverse ac Josephson effect (dc voltages developed) in transition region

Facilities: Fabrication and Characterization

development of deposition systems for thin film fabrication

operational stage:
- electron-beam deposition system w/ rotatable sources (@ Wayne State)
- rf triode sputtering system (@ Ford)
- laser ablation deposition system (w/ Kushida @ Wayne State)
- rf diode sputtering system (@ Ford)

development stage:
- dc sputtering system (@ Wayne State)
- dual ion-beam sputtering system (@ Ford)
- triple-source rf magnetron sputtering system (@ Wayne State)
- three-source electron-beam deposition system (@ Ford)

development of physical property characterizations

automation of electrical resistivity and I-V characteristics measurements (2 systems)
- N.B., special care in shielding from the earth's magnetic field and from electromagnetic radiation are incorporated in systems

complete magnetic property characterizations:
- ac susceptometer (h_{ac}=4 mOe - 10 Oe; T=2 - 150 K; f=10 - 50 kHz); χ' & χ'' measurements capability
- vibrating sample magnetometer (H_{dc}=1Oe - 1.2 kOe; T= 2 - 300 K) magnetic anisotropy effects measureable
- SQUID magnetometer (H_{dc}= 0 - 55 kOe; T= 2 - 800 K)

electromagnetic response characterizations:
- rf/microwave effects in range of MHz to GHz frequencies
- suitable cryogenic equipment and spectrometers
- millimeter wave absorption & transmission experiments

Major Accomplishments:

(i) Development of deposition systems for the fabrication of thin films from the high-temperature superconducting materials. As listed in the preceding sections, several different techniques are being developed for the fabrication of thin films. We have been successful in depositing YBaCuO films on sapphire with reproducible superconducting properties (60 K $<T_c<$ 70 K) by a sequential layering in an electron-beam deposition system and from a single YBaCuO target in a triode sputtering system. The annealing process permits some control over the width of the resistive transition region. The rapid thermal annealing process has permitted the use of Si substrates (with and without SiO_2 overlayers) with the high-T_c materials and thus the possible incorporation of semiconductor and superconductor technology. [Publications 1-3]

(ii) Systematic investigations of the magnetic response to oscillating and static magnetic fields. A comprehensive study of the magnetic response to an oscillating magnetic field through χ_{ac} measurements in bulk materials (dimensions >> λ_L=penetration depth) and thin films indicates a direct correlation of the microstructure (Josephson) coupling to the critical current. The magnetic response in these granular structured networks is successfully modeled to the magnetic flux developed in a superconducting ring with a single weak link (Josephson junction). Thus the weakest link in these coupled systems dominates the magnetic effects observed in these materials, including the strong field dependence and the nonlinear response to the field. Strong magnetic anisotropic effects in films also have been observed in both ac and dc measurements which require further investigations. [Publications 4-5]

(iii) Dynamic response to electromagnetic radiation. The reverse ac Josephson effect experiments have clearly demonstrated the appearance of sizeable dc voltages (10 μV) being developed in these granular films without any biasing. The increase in the dc voltages occurs in the transition region where the coupling is the poorest and thus allowing the finite voltage states to be more readily accessible for low rf power. In addition, several dynamical features have been observed with the application of microwave radiation. For example in I-V measurements, the zero-voltage vertically-sloped line is shifted to finite voltages in the presence of weak electromagnetic fields and usually is accompanied by a negative slope for both positive and negative currents. These features may be due to soliton propagation or some other novel physics. More systematic investigations are being pursued to elucidate these features. [Publications 6-7]

PUBLICATIONS

Thin films:

1. "Deposition and characterization of superconducting YBaCuO films," E.M. Logothetis, R.E. Soltis, R.M. Ager, W. Win, C.J. McEwan, K. Chang, J.T. Chen, T. Kushida, and L.E. Wenger, Physica C **153-155**, 1439-1440 (1988).

2. "Rapid thermal annealing of YBaCuO films on Si and SiO_2 substrates," M. Aslam, R.E. Soltis, E.M. Logothetis, R. Ager, M. Mikkor, W. Win, J.T. Chen, and L.E. Wenger, Appl. Phys. Lett. **53**, 153-155 (1988).

3. "Superconducting and Josephson properties of YBaCuO thin films," T. Kushida, K. Chang, L-X Qian, W. Win, J.T. Chen, L.E. Wenger, E.M. Logothetis, R.E. Soltis, and D. Ager, Proceedins of the International Conference on Advanced Materials (Jpn.), to be published.

Josephson coupling effects:

4. "Interfacial coupling dependence upon the superconducting properties of metallic and insulating YBaCuO composites," L.E. Wenger, W. Win, J.T. Chen, J. Obien, M. Wali, M.Bhullar, E.M. Logothetis, R.E. Soltis, and D. Ager,Physica C **153-155**, 353-354 (1988).

5. "The complex ac susceptibility-critical current relationship in oxide superconductors," L.E. Wenger, W. Win, C.J. McEwan, J.T. Chen, E.M. Logothetis, and R.E. Soltis, in <u>High-Tc Superconductors</u>, ed. by H.W. Weber, (Plenum, New York, 1988), p. 601.

Microwave & millimeter wave effects:

6. "Microwave effects in Josephson-coupled high-temperature granular oxide superconductors," J.T. Chen, L.E. Wenger, E.M. Logothetis, C.J. McEwan, W. Win, R.E. Soltis, and R. Ager, Chinese J. Phys. **26**, S93-S98 (1988). (invited paper)

7. "Millimeter-wave absorption in LaBaCuO and YBaCuO superconductors," A.T. Wijeratne, G.L. Dunifer, J.T. Chen, L.E. Wenger, and E.M. Logothetis, Phys. Rev. B **37**, 615-618 (1988).

Proposed Program for 1988-89

(1) Continuation of thin film fabrication and physical characterization with further development of other deposition systems at Wayne State and Ford.

(2) Fabrication of thin films of newer high-temperature superconducting materials.

(3) Improvement of superconducting properties and microstructural characteristics in these films.

(4) Fabrication of Josephson junction(s) in controllable fashion.

(5) Studies of the electromagnetic response of these granular films as to the suitable/feasibility as radiation detectors and electromagnetic shields.

(6) Studies of electrodynamic behavior of films in the presence of microwave and infrared fields. This is especially beneficial in understanding the nature of the high-temperature superconductivity, the Josephson properties, and other novel properties that can be associated with small coherence length superconductors ($\xi \ll \lambda_L$).

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DEPOSITION AND CHARACTERIZATION OF SUPERCONDUCTING YBaCuO FILMS

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Films of $YBa_2Cu_3O_y$ have been prepared on sapphire substrates by rf sputtering from a single nonconducting target made by hot-pressing unreacted powders of Y_2O_3, $BaCO_3$ and CuO and by e-beam deposition of multilayers of Cu, Y and BaF_2. After post-growth annealing in oxygen, these films exhibited superconducting properties with T_c onsets above 90 K and with zero resistances and diamagnetic susceptibilities above 60 K. Resistivity, ac magnetic susceptibility and reverse ac Josephson effect measurements indicate a very weak Josephson coupling between the superconducting grains of these polycrystalline films.

1. INTRODUCTION

Since the first application of the high T_c superconductors is expected to be in electronics, a large effort has been devoted during the past year to the preparation of YBaCuO films. Many different deposition techniques have been explored including e-beam evaporation, sputtering, MBE, laser evaporation and metallorganic deposition. Although most of these techniques have recently given single crystal or highly oriented films on special substrates (single crystal $SrTiO_3$, MgO and ZrO_2) with critical current densities in excess of 10^6 A/cm^2, these films are still not of device quality. Furthermore, films grown on technologically more important substrates, e.g. Si, SiO_2, Al_2O_3, have inferior properties. Consequently, additional effort is needed to understand the problems and improve the properties of the films. In this paper, we report some results on the preparation of YBaCuO films on sapphire subtrates by two techniques, rf triode sputtering from a single composite target and multilayer deposition by an e-beam gun using BaF_2 as the source for Ba.

2. EXPERIMENTAL PROCEDURES

2.1. Film Preparation

Sputter deposition from a single target was carried out with a magnetically enhanced rf triode sputter source. The target was prepared by hot pressing unreacted Y_2O_3, $BaCO_3$ and CuO powders at 900°C and 8000 psi. The powders remained essentially unreacted but were highly compacted with less than 5% porosity. The disk was sufficiently strong to be machined to the required target dimensions. The substrates, were heated during deposition up to 450°C. Argon with 1 to 3% oxygen was used as the sputtering gas and the deposition rate was on the order of 100 Å/min.

Electron beam deposition was done with a single gun with three hearths containing Y, Cu and BaF_2. The three sources were used sequentially to deposit one or more five-layer (Cu-BaF_2-Y-BaF_2-Cu) units corresponding to the stoichiometric YBa_2Cu_3 composition. The sapphire substrates were not heated and no oxygen gas was used during deposition. The deposition rates were on the order of 600 Å/min. Post annealing of these films was carried out in flowing oxygen and water vapors needed to remove fluorine from the films.

2.2 Measuring Techniques

The films were characterized by x-ray diffraction, SEM and RBS. The resistance of the films was measured by standard four-contact dc and ac techniques. The ac magnetic susceptibility was measured with a mutual inductance technique with an ac measuring frequency of 250 Hz and ac driving field varying from 4.2 mOe to 4.2 Oe.

3. RESULTS AND DISCUSSION

3.1 Sputtered Films

All films discussed here were prepared from a hot-pressed composite target with Y, Ba, Cu ratio of 1:2:3. The as deposited films on sapphire (unheated or heated up to 450°C) were amorphous and highly resistive. A subsequent anneal in oxygen made the films superconducting. Figure 1 shows typical results on the resistivity of a 3-micron thick film annealed at 870°C for one hour and slowly cooled to room temperature. The onset of superconductivity occurs above 90 K but zero resistance is obtained at considerably lower temperatures in the range 60 to 70 K. These results are similar to those obtained by others (1,2). Annealing at temperatures higher than 870°C makes the superconducting transition broader. X-ray diffraction showed that the films were polycrystalline without preferential orientation, containing mostly the orthorhombic $YBa_2Cu_3O_y$ phase and small amounts of Y_2BaCuO_5 and other unidentified phases. X-ray fluorescence indicated that the sputtered films were deficient in Cu by

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(North-Holland Physics Publishing Division)

about 20%. This result is consistent with the presence of the Y_2BaCuO_5 phase in the films and with previous reports (1,2). This Cu deficiency may be one reason for the low $T_c(0)$ found in these films. This is consistent with the finding that some films grown on $SrTiO_3$ and ZrO_2 substrates also have $T_c(0)$ below 70 K. On the other hand, the low $T_c(0)$ may result from interaction of the films with the aluminum oxide substrate. This is being investigated further. Very dense targets consisting of unreacted materials have several advantages over powdered targets (2) or dense targets made from prereacted materials. For example, unreacted dense targets do not require the many hours of degassing and the "sputter-up" configuration of the powdered targets. Furthermore, in contrast to prereacted powders, hot pressing of unreacted powders can provide very dense large size ceramics that can be machined to the desired shape and size without fracture, especially in the case of multiphase materials.

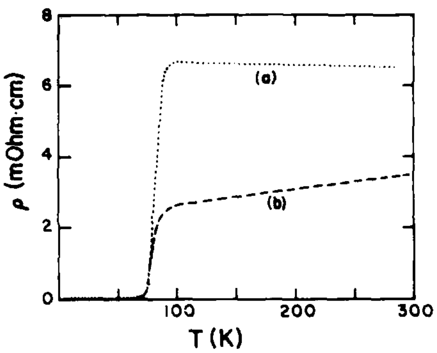

Fig. 1. The temperature dependence of the resistivity of a sputtered (a) and an e-beam deposited (b) film on sapphire.

Figure 2 shows the ac magnetic field variation of the inductive part $\chi'$of the susceptibility of the film of Figure 1 as a function of temperature. The main feature of these results is the strong dependence of χ' on the magnitude of the magnetic field even for small fields. This behavior is similar to that found in polycrystalline single-phase and multiphase YBaCuO materials (3). It can be understood qualitatively by considering the film as a granular superconductor consisting of Josephson-coupled superconducting grains (3). Comparison of the magnetic behavior of the films in this study with that of the bulk materials in Ref. 3, suggests that the Josephson coupling in the films is very weak. The reason for this behavior is presently under investigation. The granularity of the films is also demonstrated by reverse ac Josephson experiments. A large dc voltage is measured between two contacts on the film upon the application of a microwave field at temperatures below 80-90 K.

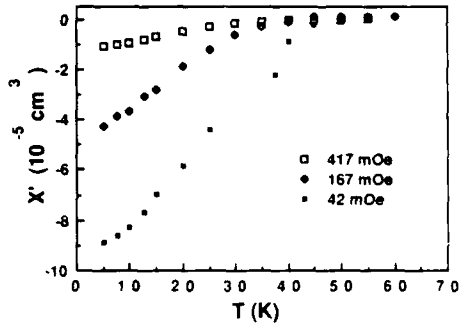

Fig. 2. The inductive χ' susceptibility as a function of temperature for the sputtered film of Fig. 1.

3.2 Electron-Beam Deposited Films

Figure 1 shows typical results on the temperature dependence of the resistivity of films e-beam deposited on sapphire. The film in this figure, which is 0.69 micron thick and consists of one unit of the Cu-BaF_2-Y-BaF_2-Cu layers, was annealed at 850°C for one hour, cooled slowly to 550°C, annealed at this temperature for one hour and then slowly cooled to room temperature. RBS studies indicate that, after annealing, the five layers have mixed well. The properties of the e-beam deposited films are similar to those of the sputtered films and also comparable to those obtained previously with sapphire substrates using the same deposition method with pure Ba or BaO as source for Ba (4). Preliminary results indicate that the multilayer technique with BaF_2 is applicable even with several micron-thick layers. Magnetic susceptibility data suggest that the Josephson coupling between superconducting grains in these films is also very weak.

4. CONCLUSIONS

This work shows that dense sputtering targets made from unreacted powders can provide sputtered films of $YBa_2Cu_3O_y$ with properties similar to those of films prepared from ceramic $YBa_2Cu_3O_y$ targets or from powdered targets. In addition, it is found that BaF_2 can be successfully used in the multilayer deposition technique. Finally, ac magnetic susceptibility measurements indicate a very weak Josephson coupling between superconducting grains of $YBa_2Cu_3O_y$ films grown on sapphire substrates.

REFERENCES

(1) M. Hong et al., Appl. Phys. Lett. 51, 696 (1987).
(2) P. H. Ballentine et al., MRS Fall Meeting, Boston, Nov. 30, 1987.
(3) L. E. Wenger et al., this conference.
(4) B-Y. Tsaur et al., Appl. Phys. Lett. 51, 858 (1987).

Rapid thermal annealing of YBaCuO films on Si and SiO_2 substrates

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A very rapid thermal annealing technique has been employed on sputter-deposited YBaCuO films. After an O_2 anneal (with or without a N_2 preanneal) at temperatures as high as 920 °C for 8–12 s, films on (100)Si and on SiO_2/Si substrates exhibited superconductivity onsets above 95 K and zero resistance in the range 40–66 K.

The discovery of the high T_c metal oxide superconductors[1,2] has generated a great deal of excitement because of the many potential applications of these materials. Since the first of these applications is expected to be in electronics, a large effort has been devoted to the preparation of thin YBaCuO films. During the past year, many different deposition techniques have been studied,[3] including electron beam evaporation, sputtering, molecular beam epitaxy, laser evaporation, and metalorganic deposition. Most of these techniques have been successfully used to grow superconducting films on special substrates such as single-crystal $SrTiO_3$, MgO, and ZrO_2 with critical current densities in excess of 10^6 A/cm^2 at 77 K. In general, the as-deposited films are nonsuperconducting and require a post-growth anneal in oxygen. Typical annealing temperatures are in the range 700–950 °C with annealing times from a few minutes to 1 h. In contrast to special substrates, films grown on technologically more important substrates, e.g., Si and SiO_2, have inferior properties.[4–7] Typically, films deposited directly on Si or SiO_2 show very broad transitions with $T_c(0)$ below 30 K for Si substrates and below 40 K for SiO_2 substrates. Studies[6,7] suggest that the poor quality of these films is due to the severe interaction between the films and the Si or SiO_2 substrates. Several research groups[7–9] have investigated the use of a buffer layer (e.g., ZrO_2, and Ag) between the YBaCuO films and the Si or SiO_2 substrates to suppress the diffusional effects. The most successful results appear to be those obtained by Mogro-Campero and Turner,[9] who very recently reported $T_c(0) = 83$ K for furnace-annealed films on SiO_2/Si substrates with a ZrO_2 buffer layer. However, it is still desirable to develop the capability to deposit good superconducting YBaCuO films directly on Si and SiO_2 substrates. In this letter, we report initial results of a special rapid thermal annealing procedure that provides YBaCuO films directly on Si and SiO_2/Si substrates with improved superconducting properties.

All the films discussed in this letter were prepared by sputtering from a single target using a magnetically enhanced rf triode sputter source. The target was prepared by hot pressing at 900 °C and 8000 psi unreacted Y_2O_3, $BaCO_3$, and CuO powders in proportion corresponding to the stoichiometric $YBa_2Cu_3O_y$ composition. The powders remained essentially unreacted, but were highly compacted with less than 5% porosity. For most of the work, argon with 1–3% oxygen was used as the sputtering gas at a pressure in the range 1–10 mTorr. The deposition rate was on the order of 100 Å/min. The films were characterized by x-ray diffraction, scanning electron microscopy, transmission electron microscopy, and x-ray fluorescence. The resistance of the films was measured by standard four-contact dc and ac techniques. Currents in the range 1–100 μA were used, and the minimum voltage detectable was on the order of 10 nV. Our zero resistivity corresponds to resistivity values of less than 10^{-7} Ω cm.

Most of our work has been done with films on single-crystal sapphire, Si, and SiO_2 on Si substrates. Some results on the electrical and magnetic properties of films deposited on sapphire have been already reported.[10] For sapphire substrates heated to 450 °C, it was found that post-growth annealing in O_2 in the range 800–900 °C for times ranging between a few minutes to 1 h resulted in films with an onset of superconductivity above 95 K and zero resistance at considerably lower temperatures in the range 60–70 K. These results are similar to those obtained by others.[11,12] Annealing at temperatures higher than 870 °C makes the superconducting transition broader. X-ray diffraction showed that the films were polycrystalline without preferential orientation, containing mostly the orthorhombic $YBa_2Cu_3O_x$ phase and small amounts of Y_2BaCuO_5 and other unidentified phases. Electron microscopy studies showed considerable inhomogeneity in these films with several phases other than the 123 material, including Y-rich phases and the 211 phase. X-ray fluorescence indicated that the sputtered films were deficient in Cu by about 20%. This Cu deficiency is consistent with the presence of Y_2BaCuO_5 and Y-rich phases in the films and with previous reports.[11–13] Following our initial studies, it has been established that successful sputtering from a single target requires excess Cu in the target so that the deposited films are not Cu deficient with degraded superconducting properties. This conclusion is also consistent with our finding that some films grown on $SrTiO_3$ and ZrO_2 substrates also have $T_c(0)$ below 70 K.

In our study, all Si wafers used as substrates were piranha cleaned and HF etched; they were sealed in a class 100 clean room and were transferred into the sputtering unit just before deposition. The Si substrates were not heated during

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deposition but their temperature was somewhat elevated (100–150 °C) because of plasma heating. When a conventional furnace annealing procedure similar to the one described above for sapphire substrates was used for films deposited on Si and on SiO_2/Si substrates, the films did not become superconducting. Instead the resistance of the films increased rapidly with decreasing temperature down to 4.2 K. This behavior is similar to that observed by others under similar conditions of preparation and was shown to arise from rapid diffusion of Cu, Ba, and Si.[6]

In an attempt to minimize the interaction between the film and the substrate, we investigated the use of a light-powered rapid thermal processor employed in Si device technology. This processor can heat a Si wafer to temperatures higher than 900 °C in less than 5 s and allow cooling to 200–300 °C in less than 20 s. Figure 1 shows the temperature dependence of the resistivity of a 2-μm-thick film deposited on an unheated Si wafer after rapid thermal annealing. After deposition, the film was dark but highly resistive. The O_2 anneal of the film in Fig. 1 consisted of a heating time of 5 s to 920 °C, annealing at this temperature for 8 s, and cooling to room temperature in about 80 s. The onset of superconductivity of this film is at about 95 K with zero resistance occurring at about 46 K. Most of the samples annealed under these conditions showed very similar behavior. However, annealing times longer than 35 s at 920 °C changed the color of the films to dark green because of the formation of the 211 phase (possibly due to the rapid diffusion of Cu and Ba) and markedly degraded the superconducting properties. The temperature dependence of the resistivity of these films indicated semiconducting behavior. It is apparent from Fig. 1 that the very rapid thermal processing employed here results in substantially improved YBaCuO films on Si. The presence of different slopes in the transition region that delay the occurrence of the zero resistance point is at least partly due to the Cu deficiency of our films sputter-deposited from the single stoichiometric YBa_2Cu_3O source. It is expected that with a stoichiometric $YBa_2Cu_3O_y$ film obtained by using a Cu-rich target in a single-source sputtering system like ours, or by appropriately adjusting the fluxes in a multiple-source deposition system, the very rapid thermal annealing will lead to films on Si with higher $T_c(0)$.

The properties of $YBa_2Cu_3O_y$ films on SiO_2 were studied by preparing 500-Å-thick SiO_2 films on Si by oxidation of Si wafers in dry oxygen at 1000 °C. Post-oxidation anneal of the SiO_2 films was carried out in N_2 for 30 min, and the high-temperature processing in the clean room was terminated with the saturation of the silicon oxide through a short O_2 anneal for 30 s.[14] The deposition procedure for the YBaCuO films was similar to the one used for Si substrates. After a rapid thermal annealing of the films in O_2 at 920 °C for 10 s, the $T_c(0)$ was found to be above 45 K as shown in Fig. 2(a) for a typical film. Furthermore, we found that if the films were treated in N_2 at 500 °C for approximately 30 s before the O_2 anneal, the $T_c(0)$ improved substantially as shown on Fig. 2(b). The onset for superconductivity is above 95 K and $T_c(0)$ is about 66 K. The improvement in T_c by the N_2 preanneal has also been reported[15] for $Y_{1.2}Ba_{0.8}CuO_4$ bulk samples, where it was found that a conventional furnace N_2 preanneal resulted in a sharper superconducting transition. The reasons for the beneficial effect of the N_2 anneal are presently being investigated by microstructural studies. Our results for YBaCuO films directly on Si and SiO_2/Si appear to be better than previously reported results for films on such substrates without the use of intermediate buffer layers.

In summary, our preliminary results show that a very rapid annealing schedule with times in the range of seconds rather than minutes or hours, and especially with a short N_2 preanneal, can provide YBaCuO films on Si and SiO_2 with substantially improved transition temperatures. It is expected that films with adequate Cu content will show even better superconducting properties. We are presently improving our system in order to remedy the Cu deficiency and to proceed with our investigation of the capabilities of the very rapid thermal annealing (with different gas atmospheres) to pro-

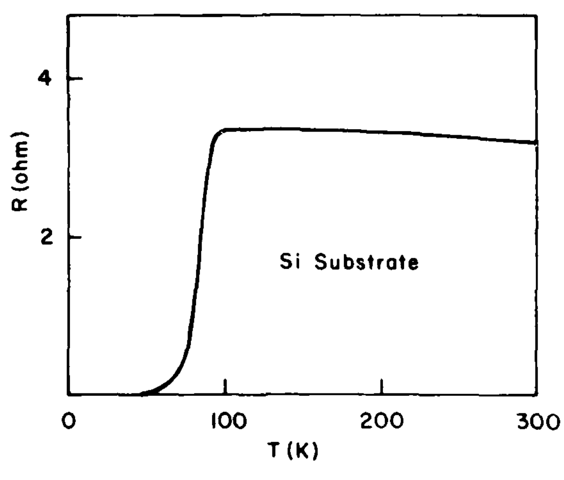

FIG. 1. Temperature dependence of the resistance of a 2-μm-thick YBaCuO film deposited on a (100)Si wafer after rapid thermal annealing in oxygen at 920 °C for 8 s; $T_c(0) = 46$ K.

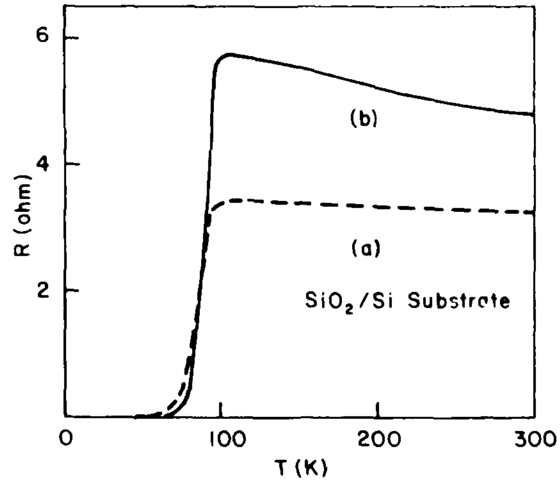

FIG. 2. Temperature dependence of the resistance of YBaCuO films on SiO_2/Si substrates: (a) after rapid thermal annealing in oxygen at 920 °C for 10 s; $T_c(0) = 50$ K. (b) after annealing in nitrogen at 500 °C for 30 s followed by an anneal in oxygen at 920 °C for 10 s; $T_c(0) = 66$ K.

[illegible] high quality YBaCuO films on Si and SiO_2/Si substrates.

We thank W. Trela, H. Blair, and E. Cartwright for the hot pressing of the YBaCuO target. The work at Wayne State University was supported by the Wayne State University Institute for Manufacturing Research, Wayne State University Industrial Productivity and Products Research Institute, and the Office of Naval Research (grant No. N000T4-88-K-09191).

[1] J. G. Bednorz and K. A. Miller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] See, for example, *Materials Research Society Symposium Proceedings Vol. 99*, edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa and H. L. Tuller (Materials Research Society, Pittsburgh, 1988), pp. 289–343 and 673–735.

[4] T. Aida, T. Fukuzawa, K. Takagi, and K. Miyauchi, Jpn. J. Appl. Phys. **26**, L1489 (1987).

[5] C. Chang, C. C. Tsuei, C. C. Chi, M. R. Schuermann, and J. P. Berosh, *Materials Research Society Symposium Proceedings Vol. 99*, edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, 1988), p. 315.

[6] M. Gurvitch, and A. T. Fiory, Appl. Phys. Lett. **51**, 1027 (1987).

[7] S. Y. Lee, B. Murdock, D. Chin, and T. VanDuzer, AIP Conf. Proc. No. 165, edited by J. Harper, R. Colton, and L. Feldman (American Institute of Physics, New York, 1988), p.427.

[8] M. Gurvitch and A. T. Fiory, *Materials Research Society Symposium Proceedings Vol. 99*, edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, 1988), p. 297.

[9] A. Mogro-Campero and L. G. Turner, Appl. Phys. Lett. **52**, 1185 (1988).

[10] E. M. Logothetis, R. E. Soltis, R. M. Ager, W. Win, C. J. McEwan, K. Chang, J. T. Chen, T. Kushida, and L. E. Wenger, in Proceedings of the International Conference on High Temperature Superconductors, Interlaken, Switzerland, 29 Feb.–5 Mar. 1988, paper C264.

[11] M. Hong, S. H. Liou, J. Kwo, and B. A. Davidson, Appl. Phys. Lett. **51**, 694 (1987).

[12] P. H. Ballentine, A. M. Kadin, J. Argana, and R. C. Rath, *Materials Research Society Symposium Proceedings, Vol. 99*, edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, 1988), p. 335.

[13] S. J. Lee, E. D. Rippert, B. Y. Jin, S. N. Song, S. J. Hwu, K. Poeppelmeier, and J. B. Ketterson, Appl. Phys. Lett. **51**, 1194, (1987).

[14] M. Aslam, IEEE Trans. Electron Devices **ED-34**, 2535 (1987).

[15] R. Herrmann, N. Kubicki, Th. Schurig, H. Dwelk, V. Preppernau, A. Krapf, H. Kruger, H. V. Muller, L. Rothkirch, W. Kraak, W. Braune, N. Pruss, G. Nachtwei, F. Ludwig, and E. Kemnitz, Phys. Status Solidi B **142**, K53 (1987).

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Advanced Materials, MRS, Tokyo, Japan

SUPERCONDUCTING AND JOSEPHSON PROPERTIES OF YBaCuO THIN FILMS

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ABSTRACT

The resistivity, maximum zero-voltage current, and ac susceptibility in YBaCuO films have been measured as a function of temperature. Also, the reverse ac Josephson effect and other rf/microwave effects have been also observed in the region of the superconducting transition. These results are consistent with a Josephson-coupled micrograin model for the granular high T_c superconductors.

INTRODUCTION

YBaCuO superconducting films are of great importance for understanding the physics behind the new high T_c superconductors as well as for their technical applications. We have prepared such films using electron-beam evaporation, sputtering, and laser ablation techniques on a variety of substrates. The present experimental results for current-voltage (I-V) characteristics, temperature dependence of the maximum zero-voltage current (I_0), magnetic-field dependence of the ac magnetic susceptibility (χ_{ac}), reverse ac Josephson experiments, and other rf/microwave responses are all compatible with a Josephson-type intergranular coupling model for this class of ceramic superconducting oxide films. Furthermore, it will be demonstrated that the lack of a Meissner effect observation does not preclude the existence of a superconductivity in these oxide materials.

EXPERIMENTAL PROCEDURE

The experimental results presented in this paper were obtained on films prepared by an electron-beam evaporation technique utilizing a rotatable four-source hearth. Sequential layers of Cu, BaF_2, Y, BaF_2, and Cu were deposited in stoichiometric proportions on $(1\bar{1}02)$ sapphire substrates under vacuum. Subsequently, the films were annealed at 850°C for one hour under a moist O_2 flow, slowly cooled to 550°C, annealed for another hour at 550°C, and furnace cooled to room temperature. The thickness of the annealed films was approximately one micron. An "H-shaped" film was used for four-probe resistivity and I-V characteristic measurements, while simultaneously-deposited, rectangular-shaped films were utilized in the ac susceptibility measurements and rf/microwave studies. The superconducting properties for both the "H-" and rectangular-shaped films are the same and do not appear to have changed over a period of several months.

The ac susceptibility is measured by using a mutual inductance technique[1]. The induced voltages from a pair of sensing coils wound over an excitation coil are electronically subtracted by a two-phase lock-in amplifier with the unbalanced voltage being produced by the sample in one of the two sensing coils and any background signal. The difference in unbalanced voltages when the sample is pneumatically raised and lowered between the two coils eliminates any background signals and is proportional to the susceptibility.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the resistance for a YBaCuO film deposited on a sapphire substrate. The onset temperature T_{onset} is approximately 90 K with the zero-resistance temperature $T_c(0)$ being 68 K (< 2 μohm-cm). A small current of 10 μA or less

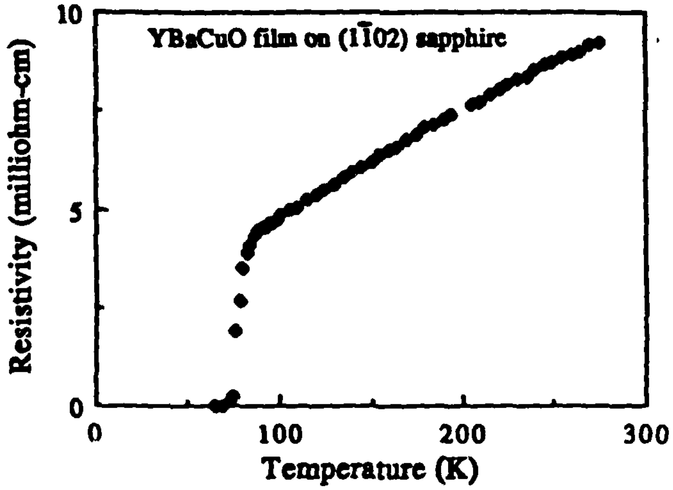

Fig. 1. The resistivity as a function of temperature for a YBaCuO film.

is used to measure the resistance of this film in order to avoid any induced magnetic field effects on the intergranular coupling. The normal-state resistance is metallic-like and changes linearly as a function of temperature, indicating the film is of good quality in terms of its conduction properties. Figure 2a indicates a well-defined maximum zero-voltage current I_0 with the temperature dependence of I_0 being shown in Figure 2b. The magnitude of the critical current and its temperature dependence of approximately $(T_c-T)^{3/2}$ suggest that the junction region between grains is more characteristic of a normal metallic barrier than an insulating one, perhaps as in a microbridge arrangement.

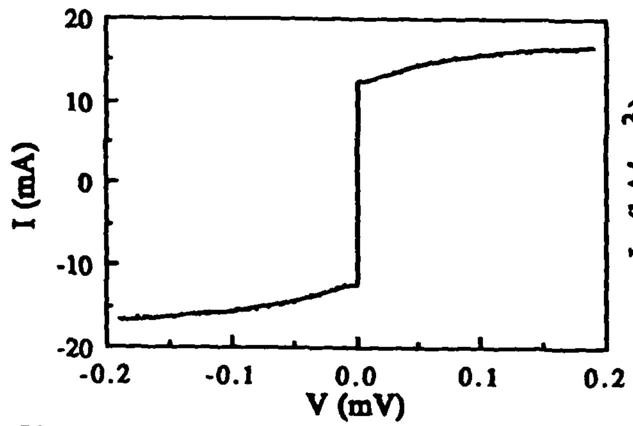

Fig. 2a. The I-V characteristics at 4.2 K of a YBaCuO film.

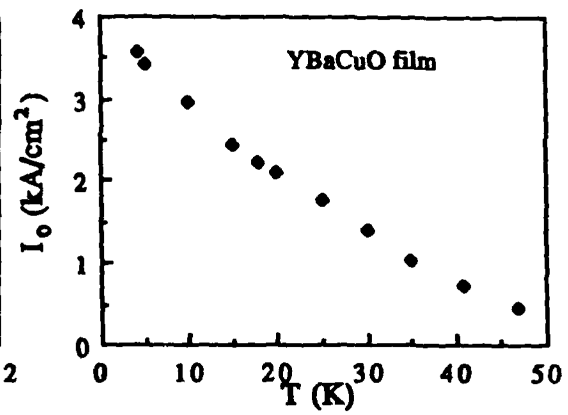

Fig. 2b. Zero-voltage current I_0 as a function of temperature.

In Figure 3, the diamagnetic (inductive) component χ' of the ac magnetic susceptibility is shown for oscillating magnetic fields ranging from 4.2 mOe to 4200 mOe and perpendicular to the plane of the film. One clearly notes that the onset of a diamagnetic signal is at a temperature of about 60 K, nearly 30 K below the temperature of the resistance decrease onset. Also the apparent Meissner (shielding) effect is strongly field dependent, and is nearly zero even in a small field of 4.2 Oe. This field dependence can be qualitatively explained in terms of a weak Josephson coupling between the superconducting grains as when the induced current from the ac magnetic field exceeds the zero-voltage current, the grains are effectively decoupled[1].

The orientational dependence of the magnetic field to the film is shown in Figure 4. For a field of 42 mOe, the χ' signal is 1000 times smaller for a film parallel to the field as compared to

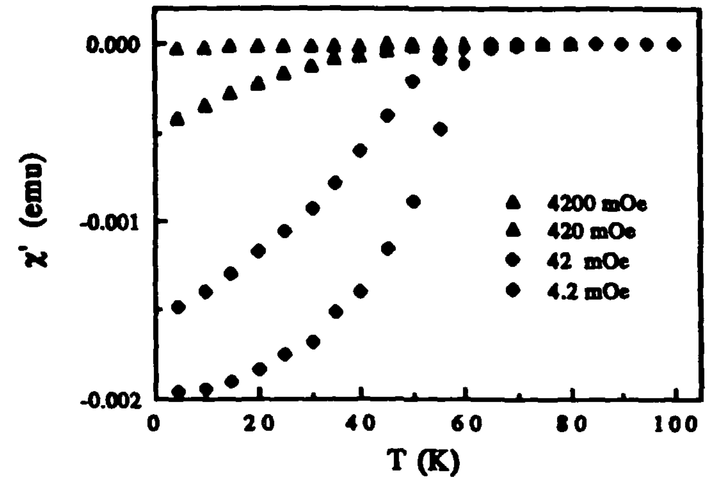

Fig. 3. Inductive component χ' of ac susceptibility as a function of the temperature for various ac magnetic fields.

the perpendicular orientation. This result clearly demonstrates one example in which the observation of the Meissner effect is a *sufficient*, rather than a *necessary*, condition for the existence of superconductivity. In other words, the observation of a Meissner effect is convincing evidence for the existence of superconductivity. However, not all superconducting materials will show the Meissner effect as it will depend upon the size, shape, dimensionality, and coupling of the granular structures. The trapping of magnetic flux as the material is cooled through the vortex state to the Meissner state in addition to the orientation and thermal history of the applied magnetic field will affect the magnitude of the Meissner effect. It may also be worthwhile to note that superconducting volume fractions estimated from field-cooled magnetization measurements are only reasonable *in a few restricted cases* where typically the materials are well-characterized in both their structural and superconducting properties. E.g., the diamagnetic response for a solid superconducting sphere with no defect structure to pin vortices would give a correct volume fraction while the diamagnetic response for a normal metallic sphere

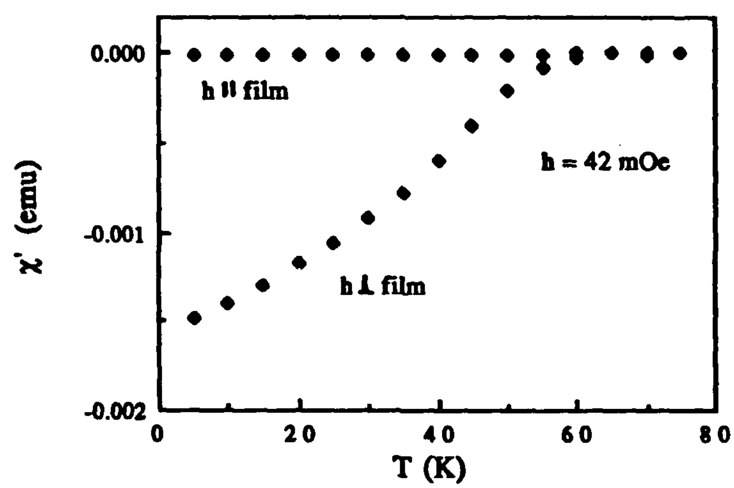

Fig. 4. The temperature dependence of the ac susceptibility χ' measured with the ac magnetic field parallel and perpendicular to the film.

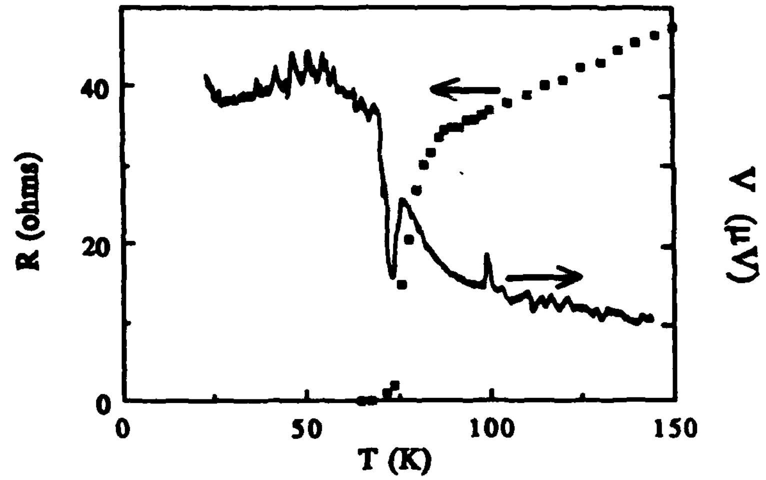

Fig. 5. The reverse ac Josephson effect observed in a YBaCuO film. The resistance vs. temperature curve is also shown.

coated with a thick superconducting layer would give rise to an overestimation of the volume fraction being superconducting.

Figure 5 shows the reverse ac Josephson effect[2] observed in the rectangular-shaped film. A three-turn, 3 mm diameter rf coil was placed next to the film with the rf field direction being perpendicular to the film's surface. Induced dc voltages generated by the intergranular Josephson junctions were measured with the same electrode configuration as for resistivity measurements. A dc voltage (20 μV) generated by the reverse ac Josephson effect is only observable below the transition region as seen on the resistance curve trace. The frequency and power level of the rf excitation were 85.5 MHz and 20 mW, respectively. It was also noted that without any applied rf excitation field, a few sharp spikes were observed in the resistivity curve near the zero-resistance transition when the resistance measuring circuitry was not properly filtered. These spikes are probably caused by stray rf fields picked up by the measuring circuit giving rise to induced voltages associated with the reverse ac Josephson effect.

CONCLUSIONS

The present work strongly supports the model of Josephson-type intergranular coupling playing an important role in the superconducting properties of the high T_c ceramic oxide thin films. The magnetic susceptibility further demonstrated that the Meissner effect observation is not a necessary condition for the existence of superconductivity.

This work is supported in part by the Office of Naval Research.

REFERENCES

1. L.E. Wenger, W. Win, C.J. McEwan, J.T. Chen, E.M. Logothetis, and R.E. Soltis, in ***High T_c Superconductors***, edited by H.W. Weber, (Plenum, New York, 1988), to be published.
2. J.T. Chen, L.E. Wenger, C.J. McEwan, and E.M. Logothetis, Phys. Rev. Lett. ***58***, 1972 (1987).

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North-Holland, Amsterdam

INTERFACIAL COUPLING DEPENDENCE UPON THE SUPERCONDUCTING PROPERTIES OF METALLIC AND INSULATING YBACUO COMPOSITES

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The superconducting and normal state properties of $Y_1Ba_2Cu_3O_7$: $Y_2Ba_1Cu_1O_5$ composites have been measured as a function of the mass ratio of the 1-2-3 to 2-1-1 oxide materials and of the sintering temperatures. As the fraction of 1-2-3 material decreases or as the sintering temperature decreases, the normal state resistivity increases from a metallic-like behavior to a semiconducting-like behavior and the magnetic-field dependence of the diamagnetic susceptibility becomes greater even though the onset of the superconductivity in the 1-2-3 material is unchanged. These results indicate that the intergrain coupling plays an important role in the physical properties and that the compositional variation in this admixture of oxide materials is a method to vary the coupling in these granular structures.

1. INTRODUCTION

The interest generated by the discovery of the high-temperature superconducting oxides (1,2) has lead to an explosion of research into the physics, chemistry, and metallurgy of these oxides. It is apparent from this research that the microstructure of these $Y_1Ba_2Cu_3O_7$ materials is important at various levels, from the twin-boundary domains at the 50 Å scale to the micron-size structure of the individual grains. Certainly the macroscopic properties, of both the bulk ceramic materials and thin films are dependent upon the interfacial coupling between the 1 to 10 micron-sized grains. This interfacial coupling between grains affects the superconducting properties similarly to a "conventional" Josephson junction in a superconducting loop. Here the term Josephson junction is loosely defined so as to include weak links and point contacts. Thus the ceramic oxide materials are pictured as multiconnected Josephson-coupled network with the Josephson junction current-voltage characteristics dominating the physical properties. The strength of the interfacial coupling is thusly determined by the microstructure which depends upon several factors, including the preparation and sintering conditions. In this paper, the interfacial effects upon the electrical and magnetic properties in composite oxide materials with varying compositional ratios of superconducting $Y_1Ba_2Cu_3O_7$ to insulating $Y_2Ba_1Cu_1O_5$ are reported through resistivity and ac magnetic susceptibility measurements.

2. EXPERIMENTAL PROCEDURES

2.1 Sample Preparation

Initially, powders of $Y_1Ba_2Cu_3O_7$ and $Y_2Ba_1Cu_1O_5$ were individually prepared by the solid-state reaction of stoichiometric mixtures of Y_2O_3, $BaCO_3$, and CuO under normal atmospheric conditions. After two anneals, the reacted powders of 1-2-3 and 2-1-1 were thoroughly mixed with mass ratios varying from 90:10 ($Y_1Ba_2Cu_3O_7$: $Y_2Ba_1Cu_1O_5$) to 50:50. These heterogeneous mixtures were then pressed into flat bars and subsequently all bars were simultaneously sintered at 975°C for 2 hours in air and cooled at a rate of approximately 50°C every 15 minutes. Only the 90:10 bar had a greyish color while the others had differing shades of green.

2.2 Measuring techniques

The resistances of the sintered bars were measured by a standard four-lead technique using either ac or dc currents of 10 μA. (Zero resistance was achieved when voltage less than 20 nV.) The ac susceptibility system measures simultaneously both the inductive χ' and resistive χ'' components of the susceptibility by a mutual inductance technique with an ac measuring frequency of 250 Hz and ac driving field varying from 4.2 mOe to 4.2 Oe. Since each of composite samples had essentially the same shape and volume (within 10%), the variation in the geometric demagnetization correction for each sample is minimized in converting the data to SI units.

3. RESULTS AND DISCUSSION

3.1 Resistivity measurements

Figure 1 shows the resistivity for five different composites of mass ratio, $Y_1Ba_2Cu_3O_7$: $Y_2Ba_1Cu_1O_5$. The effect of increasing the insulating $Y_2Ba_1Cu_1O_5$ content is clearly evident: (i) magnitude of the normal-state resistivity increases; (ii) its temperature dependent behavior changes; but (iii) the onset of the superconductivity evidenced by the initial sharp resistivity drop is the same for all composites (93 K ± 2 K). The

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normal-state resistivities for the 90:10 and 80:20 composites are approximately 11 mΩ-cm and 30 mΩ-cm respectively and temperature independent. For the other composites, the resistivity temperature-dependent behavior is more semiconducting-like although not in magnitude. Thus the addition of $Y_2Ba_1Cu_1O_3$ greatly affects the coupling between the $Y_1Ba_2Cu_3O_7$ grains in the normal state and dominates its resistive behavior. Although the 2-1-1 addition does not change the onset of superconductivity in the 1-2-3 grains, it has a strong effect on the width of the resistive transition and the corresponding zero-resistance temperature. This is shown by the long-resistive tails at the lowest temperatures which are a consequence of the experimental measuring current exceeding the maximum zero-voltage current associated with the interfacial (Josephson) coupling.

3.2 Magnetic measurements

Figure 2 shows the ac magnetic field variation of the ac susceptibility as a function of the temperature for the 80:20 composite. A diamagnetic χ' signal first appears at 92 K where the 1-2-3 grains become superconducting and then increases with a fairly weak magnetic field dependence as the temperature decreases below 90 K. At a temperature slightly lower than the zero-resistance temperature, the χ' signal at 4.2 mOe shows a rapid increase and finally attains the diamagnetic limit of -1 at the lowest temperatures. A similar qualitative behavior is observed for the other composites although the rapid increase in χ'(4.2 mOe) occurs at lower temperatures with increasing 2-1-1 material until for the 50:50 composite there is only a small increase in χ' even at 4.2 K. At a fixed temperature, the χ' signal decreases very rapidly with increasing ac magnetic field until at the largest measuring fields, a nearly field independent behavior is observed which is proportional to the amount of superconducting 1-2-3 material.

The preceding magnetic behavior can be qualitatively understood by utilizing a Josephson-coupled network model for this granular composite. As the temperature is lowered, the zero-voltage current through the Josephson junctions (i.e., the interfacial regions between superconducting grains) increases to a value comparable to the currents induced by the ac magnetic field. Thus this coupling is said to be strong enough to permit the induced currents to encompass several of the superconducting 1-2-3 grains in a circular fashion and correspondingly increase the effective area (volume) that excludes the magnetic field. This area of flux exclusion continues to increase with decreasing temperatures as the zero-voltage current increases. Finally the zero-voltage current exceeds the induced current which results in the induced current residing on the exterior surface of the sample and the diamagnetic limit being achieved.

The field dependence can be similarly understood within this model, as small magnetic fields can easily penetrate the junction region and thus decrease the net flux exclusion. In addition, small fields reduce the maximum zero-voltage current and decrease the number of interfacial regions capable of sustaining induced current(s) without resistive losses. At larger fields, the zero-voltage current is reduced to zero so that the induced currents are restricted to the individual superconducting grains.

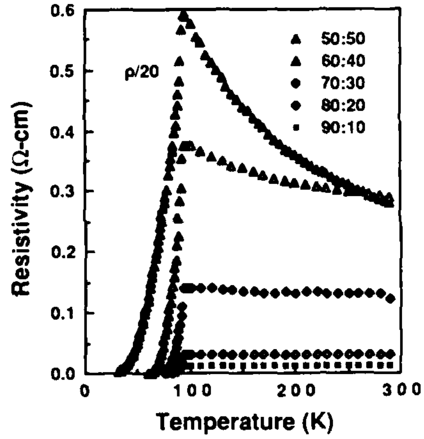

FIG.1 The resistivity as a function of the temperature for five composites of mass ratio $Y_1Ba_2Cu_3O_7$: $Y_2Ba_1Cu_1O_5$.

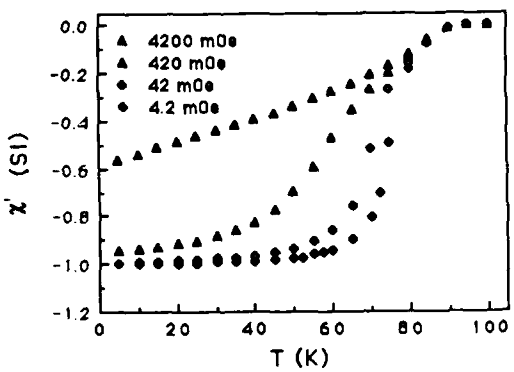

FIG.2 The inductive χ' susceptibility as a function of temperature for the 80:20 composite.

4. CONCLUSIONS

From these resistivity and ac susceptibility measurements on composites of 1-2-3 and 2-1-1 YBaCuO, the coupling between the 1-2-3 metallic superconducting grains can be effectively changed by altering the ratio of the two oxides. Increasing the 2-1-1 oxide material considerably decreases the Josephson coupling between the 1-2-3 superconducting grains and the normal-state conductivity in these composites.

REFERENCES

(1) J.G. Bednorz and K.A. Muller, Z. Phys.B 64 (1987) 189.
(2) M.K. Wu et al. Phys. Rev. Lett. 58 (1987) 908.

in: "High-T_c Superconductors",
ed. by H.W. Weber, (Plenum, New York, 1988)
Mtg. in Mauterndorf, Austria 7-11 Feb 1988

THE COMPLEX AC SUSCEPTIBILITY - CRITICAL CURRENT RELATIONSHIP IN OXIDE SUPERCONDUCTORS

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ABSTRACT

The critical currents of the high-temperature superconducting oxides (LaBaCuO & YBaCuO) in either bulk or thin film form are limited by the Josephson coupling between the superconducting grains. This coupling is also reflected in the complex ac susceptibility as a function of the ac magnetic field, h. The inductive component χ' actually consists of an ac field dependent contribution that reflects the coupling strength between the grains and an essentially field independent contribution at larger fields which represents the Meissner state of the grains. The resistive component χ'' shows a maximum that shifts to lower temperatures with increasing h and correlates with the temperature dependence of the critical current. Furthermore, the ac susceptibility data can be analyzed by assuming that these granular materials are composed of a multiconnected Josephson network which behaves coherently as a single, weakly-connected superconducting loop.

INTRODUCTION

Since the discovery of the high-temperature superconducting oxide materials of LaBaCuO and YBaCuO, a flurry of research activity has ensued. This activity has encompassed a spectrum of work ranging from fundamental research into the nature of the superconductivity to the construction of superconducting devices from these materials. Throughout this period of research, the granularity in these materials whether in bulk ceramic or thin film form has significantly affected the superconducting properties, and consequently has created some concern as to the future applicability of these superconducting oxides. One problem has been for researchers to increase the critical current density as determined by electrical measuring techniques to levels comparable to the densities deduced from magnetization-loop measurements. Thus the critical current densities may be limited by the nature of the coupling between the superconducting oxide grains and not the grains themselves.

Although current-voltage characteristics and correspondingly critical current measurements provide a measure of the strength of this coupling, measurements of the ac magnetic susceptibility as a function of temperature and magnetic field are a useful macroscopic tool for investigating the coupling in more detail, in addition to determining the critical temperature T_c. In general for a bulk superconductor (e.g. Pb or Nb), the inductive (or real) part of the susceptibility χ' goes from its diamagnetic limit of -1 (in SI units) just below T_c to zero or a small positive value above T_c indicating a weak normal paramagnetic state. The resistive (or imaginary) part of the susceptibility χ'' goes from zero just below T_c

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through a peak near T_c, to zero in the normal state. This χ'' signal is usually associated with resistive losses occuring in the vicinity of T_c as the superconductor is composed of multiconnected superconducting and normal regions. In addition, for highly conducting materials, one may actually observe negative χ' and nonzero χ'' signals even in the normal state due to eddy current effects.[1]

Since these oxide materials are granular in nature, an analysis of the magnetic properties based on the similarities to inhomogeneous superconductors would seem to be more appropriate. Previously, Ishida and Mazaki[2] studied the magnetic response in the ac susceptibility of multiconnected superconducting Tc in a porous-alumina substrate and found that both the inductive χ' and resistive χ'' components of the susceptibility were very sensitive to the ac magnetic field h. The transition width of χ' broadened as h increased although the onset temperature did not change, while χ'' had an asymmetric peak that shifted to lower temperatures as h increased. These features were well-reproduced by a phenomenological model that assumed the multiconnected network behaves like a single superconducting loop due to the coherent nature of the specimen. Since the ac susceptibility data[3-7] on the high-temperature superconducting oxide materials show a similar field sensitivity, the magnetic properties should be discussed in a similar fashion. In this paper, we report the results from our ac susceptibility measurements on a variety of oxide materials, demonstrate the dependence between the coupling and the sintering conditions, show a direct correlation between the critical current and the complex susceptibility, and extend the single loop concept to account for some additional features in the susceptibility signals.

EXPERIMENTAL

ac susceptibility

The differential (ac) susceptibility was measured by a mutual inductance technique utilizing a two-coil secondary arrangement at a driving frequency of 250 Hz and ac magnetic fields ranging from 4.2 mOe to 5.8 Oe. By using a two-phase lock-in amplifier, both the inductive component χ' and resistive component χ'' of the susceptibility could be measured simultaneously. A double-dewar apparatus permitted the temperature of the sample to be varied from 4 to 150 K while maintaining the primary-secondary coils at liquid helium, thus ensuring a constant inductive phase relationship with respect to the ac field current. A pneumatic system for raising and lowering the sample between the two secondary coils permits a determination of the absolute value of the susceptiblity. From the calibration of the susceptometer with different paramagnetic salts, the accuracy of the absolute susceptibility is approximately 1% and the relative accuracy an order of magnitude better. The susceptibility, in some cases, has been normalized into SI units, where the volume is considered to be that of the sample measured, and not of the ratio of the sample mass to the oxide's theoretical density. Since the present samples vary from bars to irregular shapes, the diamagnetic limit is attained when χ' reaches a constant value as the temperature is lowered. Also note that in the diamagnetic limit, χ'' must be zero.

Electrical characteristics

The electrical resistances of all samples were measured by a standard four-probe technique using dc or ac currents of 10 μA with zero resistance occurring at the resolution of 20 nV. This technique was readily adaptable for performing I-V characteristic measurements and the determination of the critical currents.

RESULTS

Figure 1 shows the ac magnetic field variation (fields expressed in mOe) in the in-phase χ' and the out-of-phase χ'' components of the ac susceptibility χ'-iχ'' on a $La_{1.8}Ba_{0.2}CuO_4$ sample made by the standard solid-state reaction technique. The x-ray diffraction pattern confirmed that this sample was single-phase with the K_2NiF_4 type tetragonal structure.

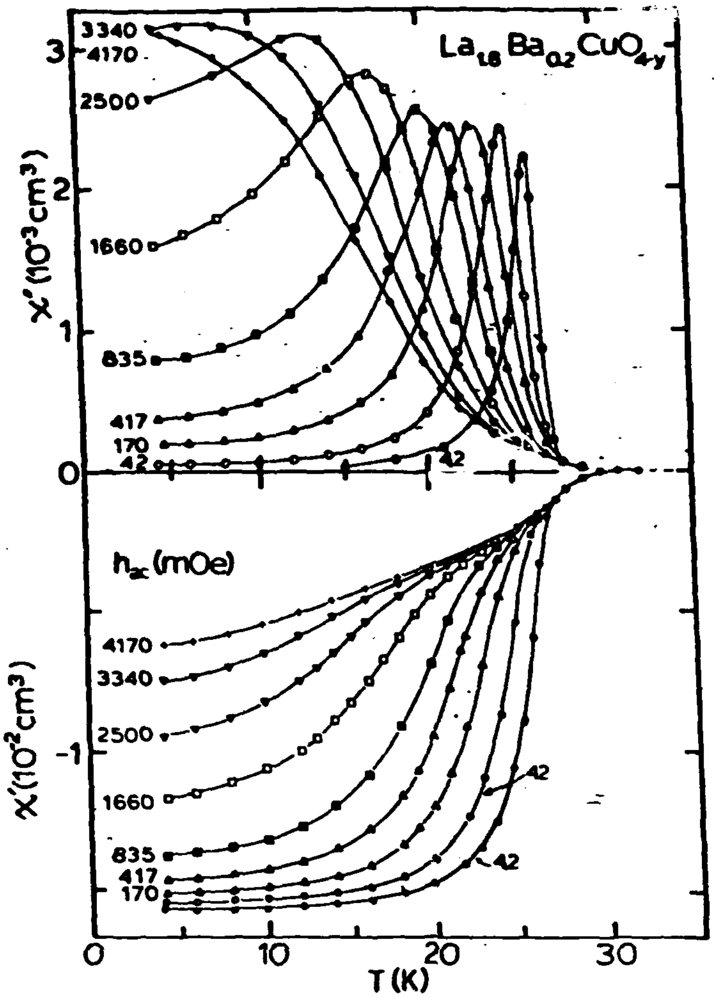

Figure 1. The inductive χ' and resistive χ'' components of the ac susceptibility for single phase $La_{1.8}Ba_{0.2}CuO_4^-$ as a function of the temperature. The ac magnetic fields are expressed in mOe (peak).

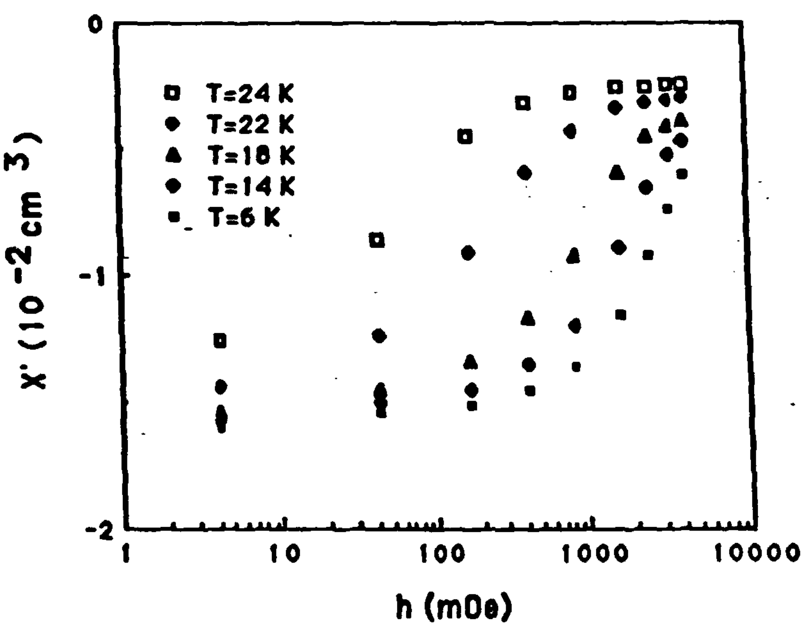

Figure 2. The magnetic field dependence of χ' for $La_{1.8}Ba_{0.2}CuO_4$ at various temperatures.

SEM photographs revealed a very porous, granular structure, with grains being typically oblong platelets and varying from 1 to 10 microns in size. The lower portion of Fig. 1 (see Fig. 2 as well) show that the inductive component χ' consists of two features: one which is extremely sensitive to the amplitude of the ac magnetic field, and the other which does not depend strongly upon the amplitude. This latter field-independence is most discernible in the temperature range of 20 to 32 K where the data converges into a single curve at the largest fields. Also note that the onset temperature of the diamagnetic χ' signal is unaffected by the field. At the lowest temperatures, the χ' signal (h=4.2 mOe) approaches the sample's diamagnetic limit; while at the largest field, the χ' value is only 1/4 of the diamagnetic limit. This value in the large-field limit is reasonable since the sample density is approximately 60% of the theoretical density for $La_{1.8}Ba_{0.2}CuO_4$, the demagnetization factors for the bulk specimen and the grains may be different, and the local field may vary due to the proximity of the grains to one another. Thus one interprets the χ' signal in the large amplitude limit as the Meissner effect of the individual superconducting material in the grains and the amplitude-sensitive signals as resulting from the shielding effect being limited by the super-current (i.e. Josephson current) between the grains. Thus the transition width reflects the strength of the coupling and the temperature dependence of the super-current.

This interpretation is consistant with the peaks observed in the resistive χ'' component. The χ'' peaks broaden and shift to lower temperatures as the field h increases although the magnitude only increases slightly. Since the χ'' signal is usually associated with energy dissipation, the maxima should occur when the induced current from the ac field exceeds the super-current and the resistive losses across the Josephson junctions are maximized. As will be shown later, the magnetic field-temperature dependence of the χ'' maxima is similar to the temperature dependence of the critical current for the bulk sample.

To further demonstrate the microscopic probe capability of the ac susceptibility measurements in relating the microstructure to the coupling in these ceramic materials, Figure 3 shows the inductive χ' component measured for a pressed ceramic composite with a 50:50 mass ratio of superconducting $Y_1Ba_2Cu_3O_7$ to insulating $Y_2Ba_1Cu_1O_5$ sintered at various temperatures. A 900°C sintering resulted in a decoupled system of the superconducting 1-2-3 grains as evidenced by a field-independent χ' for all measuring fields. (Only the 4200 mOe field result is shown.) However, a 2 hr sintering at 950°C in air produced sufficient coupling that a field-sensitive χ' is observed below 60 K. Clearly the large-amplitude χ' limit approaches that of the decoupled grains.

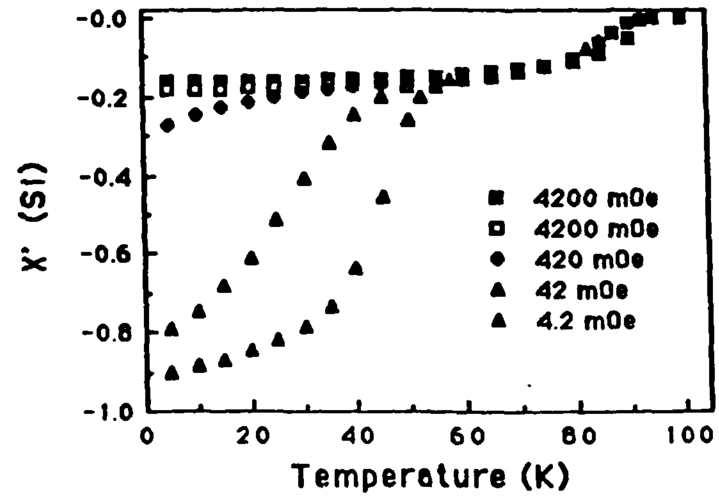

Figure 3. The inductive χ' susceptibility for a 50:50 composite of $Y_1Ba_2Cu_3O_7$ and $Y_2Ba_1Cu_1O_5$. The solid squares (■) represent χ' for the sample sintered at 900°C for 2 hrs and the remaining symbols are χ' for the 950°C/2 hr sintered sample.

MULTICONNECTED JOSEPHSON NETWORK MODEL

To understand the features described in the preceding section, we will utilize the model of a multiconnected Josephson coupled network. In a multiconnected network, a number of superconducting loops may appear for inducing current to shield against the ac magnetic field. Thus a distribution of Josephson currents should be taken into account. However, in practice, a number of such loops can be replaced by a single loop to study the magnetic field variation.[2] This is equivalent to considering that the sample behaves coherently as previously shown for 3-D granular superconductors.[8] Thus the magnetic flux ϕ generated inside a loop is given by

$$\phi = \phi_{ext} + LI$$

where ϕ_{ext} is the externally applied flux due to the ac magnetic field, L is the inductance of the ring, and I is the current through the loop. If one considers the multiconnected network to behave coherently as a single superconducting loop with a weak-link or microbridge, then the current is given by

$$I = - I_J \sin 2\pi\phi/\phi_o$$

where I_J is the maximum Josephson current and ϕ_o the magnetic flux quantum.

The solution of this nonlinear equation for ϕ is found in many textbooks usually in connection with the theory of the rf SQUID. In the limit of $2\pi LI_J >> \phi_o$, the result[2] is that the fundamental frequency susceptibility has two components and that the maximum in χ" occurs at the midpoint of the χ' transition. Furthermore, the maximum value of χ" occurs at a temperature where the induced current from the ac magnetic field is identical to the maximum Josephson current, I_J. Thus the magnetic field is proportional to the critical current at the temperature of the χ" peak with the proportionality constant be determined by the inductance L and the area of the loop. In Figure 4, we show the critical currents for the $La_{1.8}Ba_{0.2}CuO_4$ sample and a mixed phase $Y_{1.8}Ba_{0.2}CuO_4$ sample. The magnetic field-temperature loci for the χ" maxima are also displayed. By scaling the h and I_o data at one temperature, the agreement between the two sets of data is quite good.

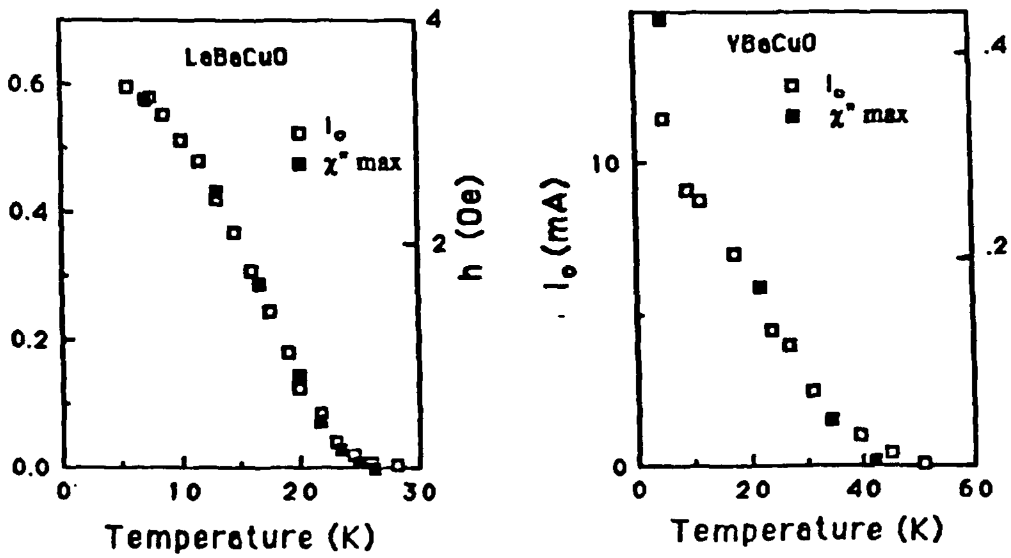

Figure 4. The critical current (▫) as a function of the temperature for single phase $La_{1.8}Ba_{0.2}CuO_4$ and mixed phase $Y_{1.8}Ba_{0.2}CuO_4$. The solid squares (▪) represent the temperature dependence of the χ" maxima for various ac magnetic fields, h.

Overall, this model qualitatively describes the magnetic behavior observed in these high-temperature superconductors. Recently, we have studied the waveforms produced from the susceptilibity coils in the vicinity of the χ'' maxima. The waveform consisted of a distorted sine wave similar to that described by Ishida and Mazaki[3] but the waveform also showed a signficant phase shift as compared to a purely inductive signal. Thus there appears to be two contributions to the χ'' signal: one due to Fourier components of the nonsinuosoidal waveform and the other due to the phase shift arising from hysteretic behavior. This latter feature can be incorporated into this model by treating the Josephson junction as a current source shunted by a resistance (1/G) and capacitance C. The current through the junction now becomes

$$I = -I_J \sin 2\pi\phi/\phi_o - G\dot{\phi} - C\ddot{\phi}.$$

It is quite apparent that the $\dot{\phi}$ term results in a 90° phase-shifted signal with respect to a purely inductive signal. The effect of these additional terms will be elaborated more fully in a subsequent paper.

CONCLUSIONS

The coupling between the superconducting grains in the high-temperature oxides materials is reflected in the field dependence of the complex ac susceptibility. These features can be interpreted within the framework of granular superconductors and are in qualitatively agreement with a model assuming the multiconnected network behaves as a coherent, Josephson coupled superconducting loop.

REFERENCES

1. R.A. Hein, *AC magnetic susceptibility, Meissner effect, and bulk superconductivity,* Phys. Rev. B 33:7539 (1986).
2. T. Ishida and H. Mazaki, *Superconducting transition of multiconnected Josephson network,* J. Appl. Phys. 52:6798 (1981).
3. Y. Oda, I. Nakada, T. Kohara, H. Fujita, T. Kaneko, H. Toyoda, E. Sakagami, and K. Asayama, *AC susceptibility of superconducting La-Sr-Cu-O system,* Jpn. J. Appl. Phys. 26:L481 (1987).
4. R.B. Goldfarb, A.F. Clark, A.J. Panson, and A.I. Braginski, *AC susceptibility measurements near the critical temperature of a Y-Ba-Cu-O superconductor,* in: "High Temperature Superconductors," D.U. Gubser and M. Schluter, eds., MRS, Pittsburgh (1987) EA-11, 261; *Evidence for two superconducting components in oxygen-annealed single-phase Y-Ba-Cu-O,* Cryogenics 27:475 (1987).
5. K.V. Rao, D.-X. Chen, J. Nogues, C. Politis, C. Gallo, and J.A. Gerber, *Frequency and field dependences of the ac susceptibility: a probe to the microstructure of high T_c superconducting materials*, in: "High Temperature Superconductors," D.U. Gubser and M. Schluter, eds., MRS, Pittsburgh (1987) EA-11, 133.
6. L.E. Wenger, J.T. Chen, E.M. Logothetis, W. Win, C.J. McEwan, R. Soltis, and D. Ager, *Josephson-coupled high temperature granular oxide superconductors,* in: "High-Temperature Superconductivity," Drexel Conference, in press.
7. H. Mazaki, M. Takano, Y. Ikeda, Y. Bando, R. Kanno, Y. Takeda, and O. Yamamoto, *Complex susceptiblity in $YBa_2Cu_3O_{6.86}$*, Jpn. J. Appl. Phys. 26:L1749 (1987).
8. J. Rosenblatt, P. Peyral, and A. Raboutou, *Phase ordering and structural disorder in bulk superconductors,* in "Inhomogeneous Superconductors-1979," D.U. Gubser, T.L. Francavilla, S.A. Wolf, and J.R. Leibowitz, eds., AIP, New York (1980) 33.

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Microwave Effects in Josephson-Coupled High Temperature Granular Oxide Superconductors

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Superconducting properties of Y-Ba-Cu-O compounds have been studied by examing the behavior of microwave induced dc voltages. The oscillatory dependences of the induced dc voltages as a function of amplitude and frequency together with the polarity reversibility indicate that these materials consist of Josephson-coupled superconducting grains. We have observed the microwave induced dc voltages in the transition region (80 – 90 K) of a single-phase $Y_1Ba_2Cu_3O_7$ sample as well as at much higher temperature (up to 240 K) in a mixed-phase $Y_{1.8}Ba_{0.2}CuO_4$ sample.

INTRODUCTION

Various superconducting transition temperatures for several copper oxides have been reported recently[1-9]. Among the well established superconducting phases, T_c values are approximately 35 K for $(La_{0.85}Ba_{0.15})_2$ CuO_4, 93 K for $Y_1Ba_2Cu_3O_7$, and 60 K for $Y_1Ba_2Cu_3O_{7-y}$ where y is approximatley 0.3. Depending upon sample preparation conditions, it is possible for a sample to have more than one superconducting phase in the same sample. For example, when a $Y_1Ba_2Cu_3O_{7-x}$ sample is prepared by rapid cooling from its annealing temperature (about 900°C), the ac susceptibility shows two distinctive steps, one with an onset temperature just above 90 K and the other at about 60 K[10]. Also, when a Y-Ba-Cu-O sample is far away from the stoichiometric 1:2:3 composition, there are indications of several superconducting transitions at higher temperatures. Since these oxide materials are granular in nature, superconductiong paths generally are weakened by the junctions formed between grains. Consequently, a resistive transition may not reach zero if

the critical currents of the individual junctions are not large enough to overcome thermal fluctuations at high temperatures. A quick estimate using $\hbar I_1/2e$, where I_1 is the Josephson current amplitude, h Planck constant, and e the electronic charge, shows that the thermal energy at 240 K is equivalent to $I_1 = 10\ \mu A$. This means that in order for a sample to achieve zero resistance, individual junction formed by grains must have a zero-voltage current much greater than 10 μA. In addition, the measurements need to be carried out with a smaller bias current and preferably in an environment in which the magnetic field is negligible[11]. For a sampel with a minority superconducting phase, the Josephson coupling is undoubtedly weak, hence it is difficult to make a complete zero resistance transition. Futhermore, multiple-connected Josephson junctions can easily trap magnetic flux even in a magnetic field free environment. Thus, it is not surprising that some transitions are not reproducible from cycle to cycle, especially at higher temperatures.

On the other hand, the reverse ac Josephson effect[12-14] is easier to observe when the Josephson coupling is weak, for example, just below the transition temperature. Otherwise, a large zero-voltage current may short out the effect. Previously, we have used rf currents to demonstrate that the reverse ac Josephson effect can exist at temperatures as high as 240 K[15]. Here we will present results of microwave experiments which clearly exhibit the oscillatory as well as the polarity reversal characteristics expected from the microwave induced dc voltage associated with ac Josephson effect.

EXPERIMENTAL RESULTS

In the reverse ac Josephson experiment, a dc voltage is induced across an unbiased junction by directly feeding an ac current of rf frequency into the junction or by radiatively coupling rf or microwave radiation. One could argue that other effects, such as the rectification by a semiconducting junction can also lead to an rf induced dc voltage. However, the characteristic behaviors of the induced dc voltage associated with the ac Josephson effect are substantially different from the more elementary semiconducting rectification effect such that the differences can be distinguished by a systematic study of the amplitude and the frequency dependences. For a Josephson junction irradiated with microwaves, the induced dc voltage is oscillatory as a function of frequency and amplitude because of its Bessel function behavior[12,13]. Alternately, it can be understood in terms of the resulting oscillatory dependence of the zero-voltage Josephson current as a function of an ac amplitude. In short, the induced dc voltage if associated with the ac Josephson effect should be oscillatory, show polarity reversible, and occur only below the superconducting transition temperature. As will be shown below, the results of our microwave experiments are consistant with the expected behaviors of Josephson junctions.

Figure 1 (a) shows the resistance versus temperature of two mixed phase Y-Ba-Cu-O samples. It has two resistance drops of nearly equal magnitude; one starting at about 240 K and the other at 90 K. Also note that there is a very small resistance anomaly at 150 K.

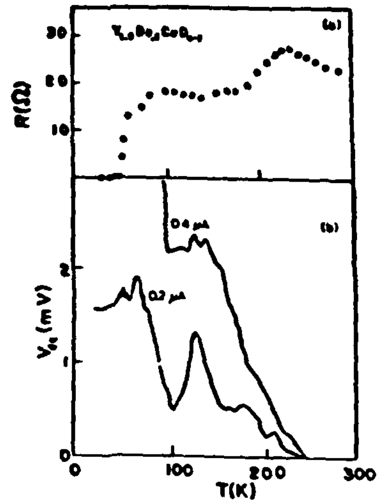

FIG. 1 (a) The resistance vs temperature of the Y-Ba-Cu-O sample used in the reverse ac Josephson experiment.

(b) The dc voltages induced by rf currents of two different amplitudes. f = 5 MHz.

However, these are not very conclusive evidence for a superconducting phase at these higher temperatures. The rf (f = 5 MHz) induced dc voltages for two different rf amplitudes are show in Fig. (1b) for the same sample. Clearly the onset of an appreciable dc voltage occurs at 240 K, the same temperature as the higher temperature resistance drop. A similar, but larger dc voltage increase occurs at 90 K, the onset of the well-established lower temperature superconducting phase. In the lower rf amplitude curve, there is additional evidence for an induced dc voltage developing at 150 K as well. Thus there appears to be significant correlation between the development of induced dc voltages from the reverse ac Josephson effect and the resistance drops.

The temperature dependence of the induced dc voltage can readily be explained as follows. (i) As the temperature decreases below the superconducting onset temperature, there is a rapid increase in the number of Josephson junctions and correspondingly the induced dc voltage increases rapidly. (ii) As the temperature further decreases, the zero-voltage currents of some junctions become larger than the rf current and thus short out some junctions. By increasing the ac amplitude, the induced dc voltage can be extended to a lower temperature. This temperature dependence and the amplitude effect can not be easily explained in terms of cracks, bad contacts or semiconducting rectification which have been proposed by some to explain resistivity drops and the rf induced dc voltages.

To study the Bessel function-like behavior and the polarity reversal, we have used microwave radiation instead of rf so that it is easier to study in the one junction regime. Figure 2 shows the induced dc voltages versus microwave amplitude for several different frequencies and at two different temperatures. Oscillations, including polarity reversals, are clearly demonstrated as a function of the microwave power. Futhermore, the dc voltage peaks shift to higher power (corresponding to higher values of the ac voltage v) as the

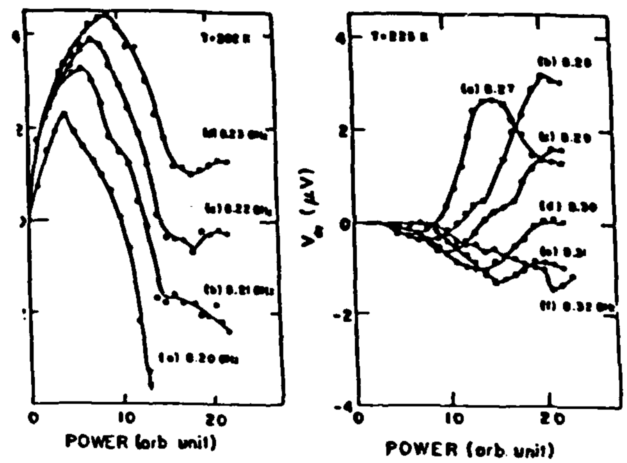

FIG. 2 Microwave induced dc voltage vs. microwave power showing oscillatory behavior. The nominal composition of the sample is $Y_{1.8}Ba_{0.2}CuO_{4-x}$.

frequency increases, in qualitative agreement with the predicted Bessel function behavior. Similar characteristics in the opposite polarity as a function of frequency were also observed as well as polarity reversal.

To verify the existence of a induced dc voltage in a well established superconductor, we performed similar measurements on a $Y_1Ba_2Cu_3O_7$ single phase sample with an onset temperature of 90 K. The results are shown in Fig. 3.

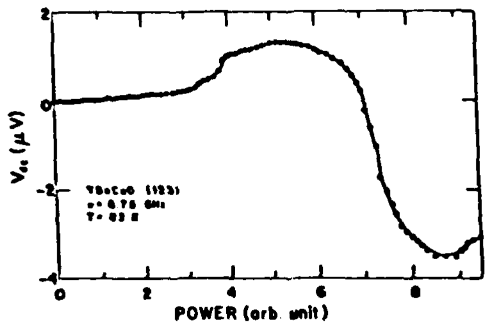

FIG. 3 Microwave induced dc voltage vs. microwave power of a single phase $Y_1Ba_2Cu_3O_7$ sample.

The frequency dependences of the microwave induced dc voltages have also been studied as shown in Figs. 4 and 5. Polarities reversals are clearly seen below the 90 K transitions as well as at temperatures as high as 204 K for a mixed phase $Y_{1.8}Ba_{0.2}CuO_{4-x}$ sample. These experimental results provide strong evidence that superconductivity exist at temperatures above 200 K.

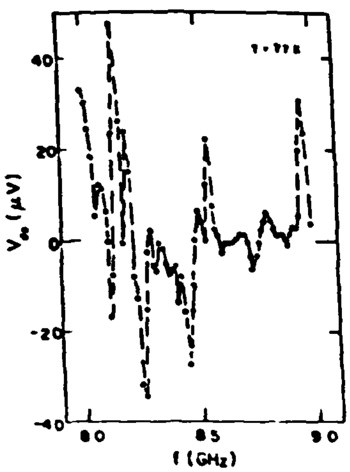

FIG. 4 Frequency dependence of microwave induced dc voltage in a $Y_{1.8}Ba_{0.2}CuO_{4-x}$ sample at 77K.

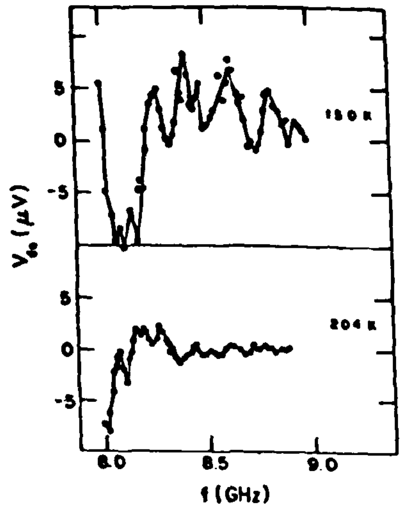

FIG. 5 Frequency dependence of microwave induced dc voltages in a $Y_{1.8}Ba_{0.2}CuO_{4-x}$ sample at higher temperatures.

REFERENCES

This work is supported by the National Science Foundation (Grant # DMR-8400711) and the Office of Naval Research.

1. J. G. Bednorz and K. A. Muller, Z. Phys. B64, 189 (1986).
2. S. Uchida, H. Tagaki, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. 26, L1 (1987).
3. R. J. Cava, R. B. van Dover, B. Batlogg and E. A. Rietman, Phys. Rev. Lett. 58, 408 (1987).
4. C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. 58, 908 (1987).
5. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. 58, 908 (1987).
6. R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. 58, 1676 (1987).
7. B. Batlogg, R. J. Cava, A. Jayaraman, R. B. van Dover, G. A. Kourouklis, S. Sunshine, D. W. Murphy, L. W. Rupp, H. S. Chen, A. White, K. T. Short, A. M. Mujsce, and E. A. Rietman, Phys. Rev. Lett. 58, 2333 (1987).
8. L. C. Bourne, M. L. Cohen, W. N. Creager, M. F. Crommie, A. M. Stacy, and A. Zettl, Phys. Lett. A120, 494 (1987).
9. R. J. Cava, presented at International Conference on High Temperature Superconductivity, July 1987 (to be published).

10. L. E. Wenger, J. T. Chen, E. M. Logothetis, W. Win, C. J. McEwan, R. E. Soltis, and D. Ager, Drexel International Conference on High Temperature Superconductivity (to be published).
11. The earth field is typically 0.5 G which can lead to a non-negligible effect if a junction loop has an area of 10^{-7} cm^2.
12. J. T. Chen, R. J. Todd, and Y. W. Kim, Phys. Rev. B5, 1843 (1972).
13. A. M. Saxena, J. E. Crow, and M. Strongin, Solid State Commun. 14, 799 (1974).
14. H. Sadate-Akhavi, J. T. Chen, A. M. Kadin, J. E. Keem, and S. R. Ovshinsky, Solid State Commun. 50, 975 (1974).
15. J. T. Chen, L. E. Wenger, C. J. McEwan, and E. M. Logothetis, Phys. Rev. Lett. 58, 1972 (1987).

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Millimeter-wave absorption in La-Ba-Cu-O and Y-Ba-Cu-O superconductors

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Millimeter-wave absorption in the new high-T_c superconducting materials La-Ba-Cu-O and Y-Ba-Cu-O has been studied at a frequency of 80 GHz over the temperature range 4–300 K and in the presence of magnetic fields 0–5.5 T. It is found that there are strong correlations between the changes in microwave absorption and the superconducting transitions at 30 K for La-Ba-Cu-O and at 90 K for Y-Ba-Cu-O samples. The Y-Ba-Cu-O samples display additional microwave features near 250 K which may be associated with a higher-temperature superconductivity.

Observations of millimeter-wave absorption in the new high-T_c superconducting materials La-Ba-Cu oxide[1] and Y-Ba-Cu oxide[2] have been made at a frequency of 80 GHz over the temperature range 4-300 K and in the presence of magnetic fields 0-5.5 T. The absorption is monitored by measuring the propagation of microwave power around samples which mostly fill a section of waveguide. The propagation displays a sudden enhancement at temperatures below T_c. For the Y-Ba-Cu-oxide samples an enhancement is noted at both $T \approx 90$ K and $T \approx 250$ K. The effect of the magnetic field is to decrease the enhancement of propagation and to reduce the temperature at which it begins.

Three types of samples having nominal compositions of $La_{1.8}Ba_{0.2}CuO_{4-x}$, $YBa_2Cu_3O_{7-x}$, and $Y_5Ba_6Cu_{11}O_x$ were investigated. All were prepared by the solid-state reaction method with Table I giving the details of the preparation conditions. An appropriate mixture of the starting materials in powder form was first heated in air. The reacted mixture was then pulverized, pressed into pellets or bars, and sintered in air. X-ray powder diffraction patterns showed for the $YBa_2Cu_3O_{7-x}$ samples a dominant single phase with identical lines to those previously seen[3] while multiple phases were seen in the $Y_5Ba_6C_{11}O_x$ samples.

Figure 1 shows a schematic diagram of the spectrometer which was used. The superconducting specimen fills a section of waveguide of length L situated between a klystron, the microwave source, and a sensitive detector. The spectrometer is a modified version of the transmission spectrometer which has been used to study the propagation of microwaves through thin metal samples.[4] The power incident on the sample can be varied with an attenuator over a range of 50 dB up to a maximum of 100 mW. The detector is a liquid-helium-cooled InSb bolometer operating in a hot-electron mode. It can be used as a straight power detector (sensitivity of 10^{-14} W) or as a homodyne mixer (sensitivity of 10^{-21} W) with the use of a microwave reference of variable amplitude and phase obtained from the original klystron. A dc magnetic field aligned with the axis of the waveguide is obtained from a superconducting solenoid in which the sample is centered. The sample is situated in a vacuum can immersed in liquid helium. The use of a heater and thermometer allows its temperature to be varied continuously between 4 K and room temperature.

The internal dimensions of the rectangular waveguide are $a = 3.10$ mm and $b = 1.55$ mm. The oxide samples are cut into the form of rectangular bars with a low-speed diamond saw and then lapped on abrasive paper to dimensions about 0.04 mm smaller than the waveguide so that they slide easily into the waveguide interior. A typical length of sample is $L = 5.0$ mm. Our observations are independent of the incident power level except for some

TABLE I. Details of sample preparation and results from x-ray powder-diffraction patterns.

Nominal composition	$La_{1.8}Ba_{0.2}CuO_{4-x}$	$YBa_2Cu_3O_{7-x}$	$Y_5Ba_6Cu_{11}O_x$
Starting materials	La_2O_3, $BaCO_3$, and CuO	Y_2O_3, $BaCO_3$, and CuO	Y_2O_3, $BaCO_3$, and CuO
Reaction temperature (°C)	900	900	900
Reaction time (h)	8+pulverizing+6	8	8
Pressure for forming pellets (psi)	8000	8000	8000
Sintering temperature (°C)	1100	900	1100
Sintering time (h)	4	8	8
X-ray powder-diffraction patterns	Single phase with K_2NiF_4-type structure and trace (<5%) of $Cu_2La_2O_5$	Single phase with other phases <2%	Multiple phases containing Y_2BaCuO_5 (dominant) $YBa_2Cu_3O_{7-x}$, $Y_2Cu_2O_5$, Y_2O_3, and CuO

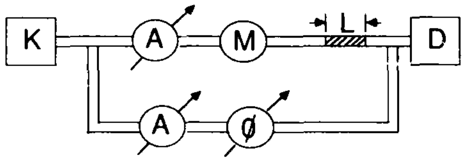

FIG. 1. Schematic representation of the spectrometer. The components include K, klystron; A, variable attenuator; ϕ, variable phase shifter; M, modulator; and D, detector.

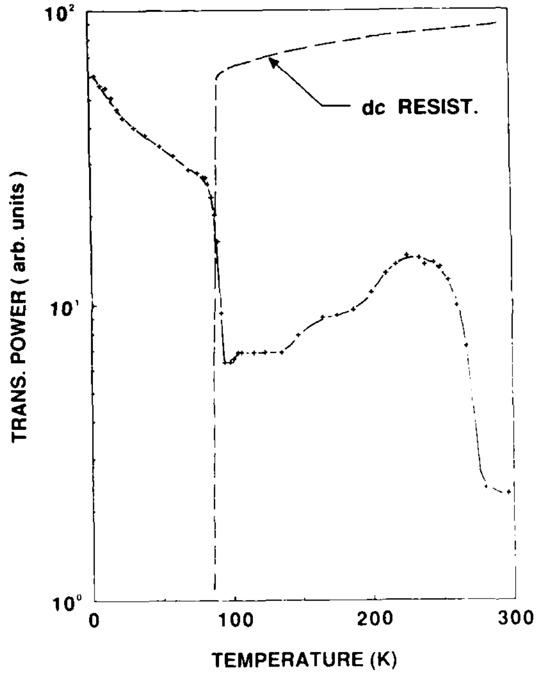

FIG. 2. Temperature dependence of the transmitted microwave power and dc electrical resistivity of a $YBa_2Cu_3O_{7-x}$ sample (both in arbitrary units on a log scale).

heating of the sample at the highest levels. At 4 K a typical reflection coefficient from the sample is 3–5 dB, whereas a typical transmission coefficient for microwave propagation *around* the sample is 10–15 dB. Thus, the sample absorbs the majority of the incident power, even though a significant amount appears at the detector. The microwave power is clearly traveling around the sample and not through it, as has been demonstrated by replacing the sample with a solid Pb sample of similar dimensions and observing a comparable power level at the detector. Also, by using electrically conducting silver paint to fill the gap between the oxide sample and the waveguide, the power level at the detector drops 150 dB or more.

The microwaves propagate down the waveguide from the klystron in the TE_{10} mode with the rf electric field perpendicular to the broad faces of the waveguide. Because the cutoff frequency for this mode, $f_c = c/2a$, is independent of b, it appears that a significant quantity of microwave power continues to propagate in the TE_{10} mode in the narrow gaps between the superconducting sample and the broad faces of the silver waveguide. In fact, the power level at the detector displays certain characteristics of a "double slit" as the frequency is changed due to variation in the interference between the two waves that propagate in the top and bottom gaps. By sealing one of the gaps with silver paint, such variations are considerably reduced.

Figure 2 shows a semilog plot of the transmitted power as a function of the temperature for a $YBa_2Cu_3O_{7-x}$ sample as well as the dc electrical resistance of the sample. T_c (measured at the midpoint of the dc resistance step) is 90 K, and the width of the transition ΔT (measured between 10% and 90% of the resistance step) is 4 K. Figure 3 shows a similar plot for a $Y_5Ba_6Cu_{11}O_x$ sample having $T_c = 91$ K and $\Delta T = 4$ K. As can be seen for both samples, with decreasing temperature there is a sharp increase in the transmitted power occurring at T_c and having a width comparable to the ΔT measured from the electrical resistance. This feature is quite stable and remains even after a large number of thermal cyclings between 4 K and room temperature. For the $YBa_2Cu_3O_{7-x}$ sample there is a similar increase in the transmitted power occurring around $T \approx 265$ K even though there is no obvious step in the resistance curve. Although no step in the transmitted-power curve is observed in this vicinity for the $Y_5Ba_6Cu_{11}O_x$ sample, there is a distinct change in the slope at $T \sim 235$ K that coincides with a change of slope in the resistance curve. These higher-temperature features are not stable and degrade considerably after a few thermal cyclings. Lack of stronger correlations at these higher temperatures could be due to the time difference in the microwave and dc resistance measurements. The similarities to those observed at the 90 K transitions, however, offer further evidence of a still higher-temperature (but unstable) superconducting transition such as reported for certain Y-Ba-Cu oxide samples from dc resistance measurements[5–7] and the reverse ac Josephson effect.[8]

Figure 4 shows the effect of a 5.5 T magnetic field on the 90 K transition in a $YBa_2Cu_3O_{7-x}$ sample. As can be seen, the magnetic field decreases the temperature at which the sudden increase in transmitted power occurs by about 3 K. It also decreases the sharpness of the power increase and continues to suppress the overall transmission coefficient even at temperatures far below T_c. We have also looked carefully for the effect of a magnetic field on the step occurring around $T = 265$ K. Such a field dependence could provide strong evidence that this step is also associated with a superconducting transition. Any such dependence, if it exists, is smaller than that observed at 90 K. Unfortunately, the present stability for our spectrometer and the reproducibility of data taken in this region are not sufficient to show unambiguously that a field of 5.5 T has a definite effect.

In Fig. 5 the temperature dependence of the transmitted power for a $La_{1.8}Ba_{0.2}CuO_{4-x}$ sample is plotted for both zero field and an applied field of 5.4 T. Also shown in the figure is the dc resistance which was measured in zero field. The features seen in Fig. 5 are very similar to those observed in the Y-Ba-Cu oxide samples. For temperatures below T_c ($\cong 30$ K), the transmitted power once again increases quite rapidly. The applied magnetic field

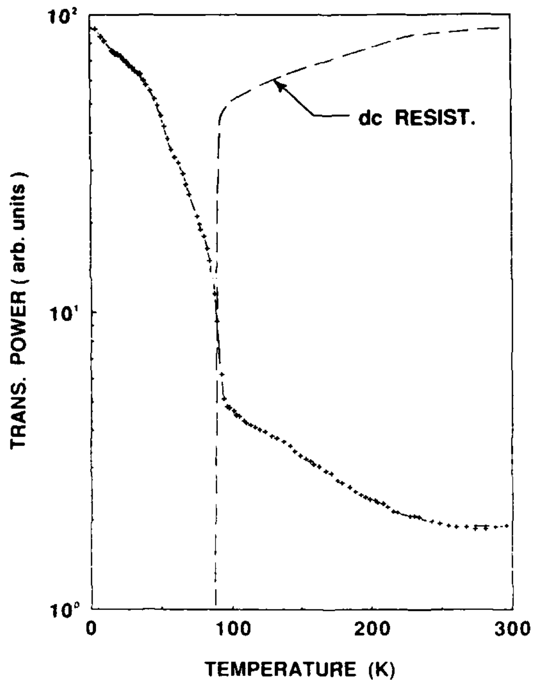

FIG. 3. Temperature dependence of the transmitted microwave power and dc electrical resistivity of a $Y_5Bu_6Cu_{11}O_x$ sample.

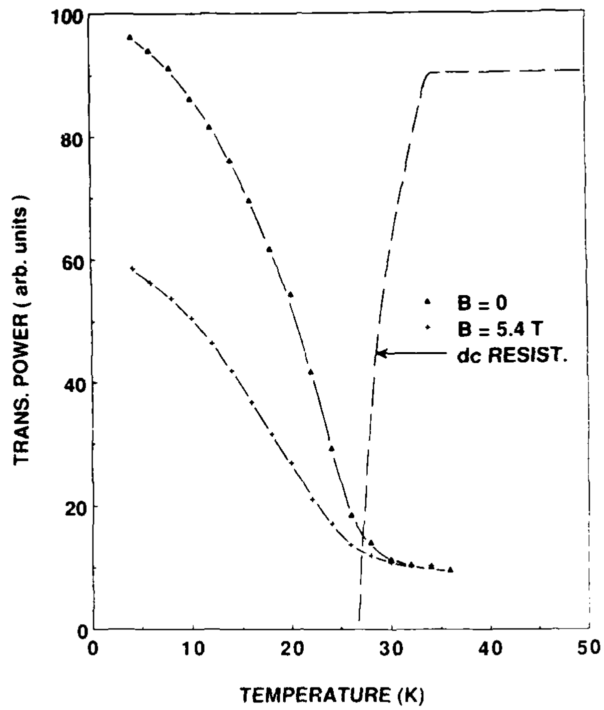

FIG. 5. Temperature dependence of the transmitted microwave power and dc electrical resistance of a $La_{1.8}Ba_{0.2}CuO_{4-x}$ sample. Also plotted is the transmitted power for an applied field of 5.4 T.

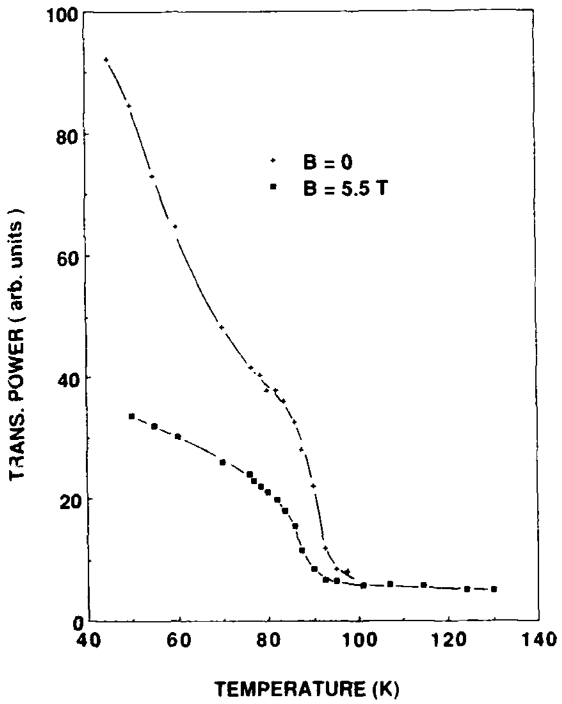

FIG. 4. Effect of a magnetic field on the temperature dependence of the transmitted microwave power for a $YBa_2Cu_3O_{7-x}$ sample.

suppresses the transmission of power at all temperatures below T_c and the sharpness of the power increment in the vicinity of T_c. By comparing Figs. 4 and 5, it is seen that a magnetic field has a similar effect on both the La-Ba-Cu-O and Y-Ba-Cu-O samples, namely an increasing suppression of the transmitted power at lower temperatures. Just the opposite would be expected for a type-I bulk superconductor due to the saturation of the superconducting properties at temperatures far below T_c. The stronger magnetic field dependence observed here at lower temperature is most likely related to a weaker superconductivity associated with Josephson coupling between superconducting grains.

The transmitted power which we measure is related to the surface impedance of the sample at microwave frequencies. For microwave propagation in the TE_{10} mode in an open waveguide of length L the transmission coefficient for the microwave fields is given by[9]

$$T=\exp\left\{-R_sL\left[1+\frac{2b}{a}\left(\frac{f_c}{f}\right)^2\right]\Big/b\left(\frac{\mu_0}{\epsilon_0}\right)^{1/2}\times\left[1-\left(\frac{f_c}{f}\right)^2\right]^{1/2}\right\}, \qquad (1)$$

where f is the frequency and R_s is the surface resistivity of the metal from which the waveguide is fabricated. Presumably, the signals we detect are described by an expression similar to Eq. (1) in which R_s is replaced by some type of weighted average of the surface resistances

of the superconducting sample and the silver waveguide. The increase in the transmission coefficient below T_c is consistent with the decrease in R_s of the superconductor which occurs at this temperature. Because an exact relation for the transmitted field and the temperature dependence of R_s for silver are unavailable, and because some residual interference between waves from the top and bottom gaps remains, we have not attempted to fit our observations to theory. Nevertheless, it is clear from the data that there are a number of features in the temperature dependence of the transmission which correlated with the characteristics of the superconducting transitions and their dependence on magnetic field.

A better method of recording this type of data (which we are now pursuing) is one with the geometry uniquely defined in which the microwaves propagate through a "single slit" down the center of the sample, both halves of which are electrically bonded to the waveguide. In this case the microwave transmission depends only on the characteristics of the superconducting material itself. Such measurements (coupled with similar measurements of the reflection coefficient) appear to offer the possibility of a sensitive determination of the electrical and magnetic properties of this class of materials consisting of granular superconductors and coupled Josephson junctions. The advantage over more traditional techniques, which make use of a microwave cavity,[10,11] appears to be a higher sensitivity and the ability to study variations in R_s over a larger dynamic range.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. H. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[4] G. L. Dunifer and M. R. Pattison, Phys. Rev. B **14**, 945 (1976).

[5] C. W. Chu, New York Times, March 10, 1987.

[6] L. C. Boume, M. L. Cohen, W. N. Creager, M. F. Crommie, A. M. Stacy, and A. Zettl, Phys. Lett. A **120**, 494 (1987).

[7] C. Y. Huang, L. J. Dries, P. H. Hor, R. L. Meng, C. W. Chu, and R. B. Frankel, Nature **328**, 403 (1987).

[8] J. T. Chen, L. E. Wenger, C. J. McEwan, and E. M. Logothetis, Phys. Rev. Lett. **58**, 1972 (1987).

[9] S. Ramo, J. R. Whinnery, and T. Van Duzer, *Fields and Waves in Communication Electronics* (Wiley, New York, 1965).

[10] W. P. Beyermann, B. Alavi, and G. Gruner, Phys. Rev. B **35**, 8826 (1987).

[11] R. Durny, J. Hautala, S. Ducharme, B. Lee, O. G. Symko, P. C. Taylor, D. J. Zheng, and J. A. Xu, Phys. Rev. B **36**, 2361 (1987). Figure 3 of this paper appears to show a temperature dependence of the microwave absorption which is opposite to our observations. The ordinate of the figure is actually a somewhat different quantity—the *derivative* of the microwave absorption with respect to magnetic field (obtained by field modulation). The temperature dependence of the absorption as determined from the cavity Q, however, is in agreement with our observations (P.C. Taylor, private communication).

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